

Structure and Reactivity of Early–Late Heterobimetallic Complexes[†]

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I. Introduction

During the past decade, coordination chemistry has seen a huge growth in novel reactions. The understanding of the effects of changes in the ligands has also led to great improvements in the direction of the

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[†] Dedicated to Professor René Poilblanc, whose seminal work on bimetallic reactivity has inspired many in the field.

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Nigel Wheatley was born in North Lincolnshire, England, in February 1973. Sixteen and a half uneventful years later, he entered the University of Cambridge to study natural sciences. He was granted his B.A. degree in 1992, having specialized in inorganic chemistry under Dr. Ron Snaith and Dr. Dominic Wright. He then went to the University of Essex to study for his Ph.D. under Professor Jon Dilworth, developing novel catalysts for the carbonylation of methanol in association with B.P. Chemicals Ltd. He wrote his thesis on phosphorus–sulfur donor complexes of rhodium and iridium in 1996. The following year, he was awarded a Marie Curie Fellowship by the European Commission, which allowed him to spend two years at the Ecole Nationale Supérieure de Chimie de Toulouse, France, studying heterobimetallic complexes and the catalysis of carbonylation reactions. Dr. Wheatley is currently working at the Universiteit Leiden, The Netherlands, modeling the active sites of hydrogenases. His other research interests include metal–metal interactions and the reactivity of coordinated ligands.

selectivity of homogeneous catalysis. Chemists are now able to finely tune the coordination sphere of a metal to obtain high selectivities in many reactions. Two recent examples include the alkoxy carbonylation of propyne to give methyl methacrylate with 99.95% selectivity,¹ and the perfectly alternating copolymerization of ethylene and carbon monoxide to give high-performance industrial polymers.²

Binuclear complexes have long been recognized to have a reactivity different from that of their mononuclear analogues.³ For instance, binuclear complexes of rhodium show outstanding catalytic activity in hydroformylation^{4,5} and in methanol carbonylation.⁶ Several stoichiometric examples show a cooperative effect between the two metal centers, e.g., the oxidative addition to diiridium(I) complexes giving d⁷–d⁷ metal–metal bonded species.⁷

Compounds which contain two very different metal centers have attracted particular interest. In recent years there has been a great increase in the understanding of the reactivity of such complexes. One example among those which will be discussed later is the reaction of heteroallenes such as CO₂ or COS with [Cp₂Zr(*μ*-N^tBu)IrCp*], giving [Cp₂Zr(*μ*-N^tBu){*μ*-OC(O)}IrCp*] and [Cp₂Zr(*μ*-N^tBu)(*μ*-S)IrCp*], respectively.⁸ In complexes such as these where one metal comes from the left-hand side of the transition series (“early”) and the other from the right-hand side (“late”), we might expect the greatest modification of reactivity over that of monometallic species. Indeed, the combination of the hard, electrophilic and oxophilic early metal center with the soft, nucleophilic late metal center can give a novel bimetallic reactivity. This has great potential in homogeneous catalysis, an important aspect of the chemistry of both



Philippe Kalck was born near Besançon, France, in 1944. He studied in Toulouse, and received his Diplôme d'Ingénieur Chimiste from the Ecole Nationale Supérieure de Chimie de Toulouse (ENSCT) in 1967. He remained in Toulouse for his doctoral research under the supervision of Professor René Poilblanc, completing his Doctorat d'Etat in 1975. Up until 1980, he combined research at the Laboratoire de Chimie de Coordination (CNRS) with teaching at the ENSCT. At that point he was appointed Professor at the Institut National Polytechnique de Toulouse (of which the ENSCT forms part), and started a research group devoted to the catalysis of carbonylation reactions that has now become the Laboratoire de Catalyse, Chimie Fine et Polymères. He is particularly attached to promoting links between industry and academia, and spent two years on secondment to Rhône-Poulenc Chimie between 1986 and 1988. His research interests include the design of highly selective catalysts and the molecular understanding of catalytic processes, fields in which he has published over 120 papers and supervised 43 Ph.D. students.

groups of metals. It also allows the modeling of strong metal–support interactions (SMSI) often seen in heterogeneous catalysts on metal oxides.^{9–11} The chemistry of early–late heterobimetallic complexes was reviewed¹² by Stephan in 1989, although, at that time, studies of reactivity, and particularly of catalysis, were few. The review of Chetcuti¹³ in 1994 is also primarily concerned with the structural chemistry of these compounds.

II. Scope of the Review

The present review covers work published from January 1988 to December 1997. It is primarily concerned with complexes in which one metal comes from group 4, 5, or 6 and the other from group 8, 9, or 10: however, the few examples of complexes where the early metal is from group 3 or the f-block and/or the late metal is from group 11 or 12 will also be covered.

III. Synthesis and Structure

In examining the literature, it is apparent that the synthesis and structural chemistry of heterobimetallic compounds are determined to a large extent by the ligands (if any) used to bind together the two metal centers. Hence, we have chosen to follow the approach of Stephan¹² and classify the complexes discussed here primarily by the bridging ligand, and not (as in the review of Chetcuti¹³) by the metal.

This is not without some difficulty, as advances in systematic nomenclature lag behind the ingenuity of synthetic chemists. For this reason, we have tried to classify the bridging ligands according to criteria which are (usually) unambiguously available from

Table 1. Unbridged Heterobimetallic Compounds

	$r(\text{M}-\text{M}')/\text{\AA}$	ref
$[(^t\text{BuO})_3\text{TiFeCp}(\text{CO})_2]$		19
$[\{\text{HC}(\text{SiMe}_2\text{NTol})_3\}\text{TiMCp}(\text{CO})_2]$ (M = Fe, Ru)	2.410(4) (M = Fe) 2.503(4) (M = Ru)	18
$[\{\text{RC}(\text{CH}_2\text{NSiMe}_3)_3\}\text{TiMCp}(\text{CO})_2]$ (R = Me, Ph; M = Fe, Ru)	2.441(5) (M = Fe) 2.527(1) (M = Ru)	18
$[(\text{Me}_2\text{N})_2(\text{C}_6\text{H}_3\text{Me}_2\text{O})\text{TiRuCp}(\text{CO})_2]$		31
$[(\text{Me}_2\text{N})(\text{C}_6\text{H}_3\text{Me}_2\text{O})_2\text{TiRuCp}(\text{CO})_2]$	2.573(1)	31
$[(\text{Me}_2\text{N})\text{Cp}^*\text{TiRuCp}(\text{CO})_2]$		30
$[\{\text{MeSi}(\text{SiMe}_2\text{NTol})_3\}\text{MM}'\text{Cp}(\text{CO})_2]$ (M = Ti, Zr, Hf; M' = Fe, Ru)	2.460(1) (M = Ti; M' = Fe) 2.605(2) (M = Zr; M' = Fe)	16
$[(\text{Me}_3\text{SiNCH}_2\text{CH}_2\text{NSiMe}_3)\text{Zr}\{\text{MCp}(\text{CO})_2\}_2]$ (M = Fe, Ru)	2.665(2), 2.664(2) (M = Fe) 2.7372(7), 2.7452(7) (M = Ru)	17
$[(^t\text{BuO})_3\text{TiCo}(\text{CO})_3\text{L}]$ (L = CO, PPh ₃)		19, 22
$[(\text{RO})_3\text{TiCo}(\text{CO})_4]$ (R = ^t Bu, ⁱ Pr, Ph, CH(CF ₃) ₂)	2.565(2) (R = ^t Bu)	22, 23
$[\{\text{HC}(\text{SiMe}_2\text{NTol})_3\}\text{TiCo}(\text{CO})_3(\text{PR}_3)]$ (R = Ph, Tol)		18
$[\{\text{RC}(\text{CH}_2\text{NSiMe}_3)_3\}\text{TiCo}(\text{CO})_3\text{L}]$ (R = Me, Ph; L = PPh ₃ , PTol ₃)		18
$[\{\text{MeSi}(\text{SiMe}_2\text{NTol})_3\}\text{MCo}(\text{CO})_3\text{L}]$ (M = Ti, Zr; L = CO, PPh ₃ , PTol ₃)	2.5542(10) (M = Ti; L = CO) 2.471(4) (M = Ti; L = PTol ₃) 2.7051(11) (M = Zr; L = CO) 2.6175(14) (M = Zr; L = PPh ₃)	260
$[(\text{Me}_3\text{SiNCH}_2\text{CH}_2\text{NSiMe}_3)\text{ZrCo}(\text{CO})_3(\text{PPh}_3)]$		17
$[\text{Cp}(^t\text{BuN}=\text{M})\{\text{FeCp}(\text{CO})_2\}_2]$ (M = Nb, Ta)		20
$[\text{Cp}_2(^t\text{BuN}=\text{Nb})\text{FeCp}(\text{CO})_2]$		20
$[(^t\text{BuN}=\text{M})_2\text{M}\{\text{FeCp}(\text{CO})_2\}_2]$ (M = Mo, W)		20, 21
$[\text{Cp}(^t\text{BuN}=\text{M})\text{FeCp}(\text{CO})_2]$ (M = Mo, W)		20
$[(\text{OC})_5\text{WFeMe}(\text{CO})_4]$	2.880(1)	32
$[(\text{Ph}_3\text{P})(\text{OC})_2\text{CpMoCo}(\text{CO})_3(\text{PPh}_3)]$	2.951(1)	27
$[(\text{OC})_2\text{LCpMoCo}(\text{CO})_3(\text{PPh}_3)]$ (L = CO, PPh ₃)	2.924(1) (L = CO)	26
$[(\text{OC})_3(\text{C}_5\text{H}_4\text{R})\text{MoCo}(\text{CO})_4]$ (R = Ac, CO ₂ Et)	2.935(2) (R = Ac)	34
$[(^t\text{BuN}=\text{M})_2\text{Mo}\{\text{Co}(\text{CO})_4\}_2]$		21
$[(\text{OC})_3\text{CpWCo}(\text{CO})_4]$		269
$[(\text{OC})_3(\text{C}_5\text{H}_4\text{R})\text{WCo}(\text{CO})_4]$ (R = ⁿ Bu, Ac, CO ₂ Me)		33, 34
$[(\text{OC})_3\text{CpMPt}(\text{PCy}_2\text{H})_3]$		98
$[(\text{OC})_3\text{CpMPt}(\text{CO})(\mu\text{-dppm})\text{MCp}(\text{CO})_2]$ (M = Mo, W)		43
$[(\text{OC})_3\text{TpMoCuL}]$ (L = PPh ₃ , tmen)	2.639(2) (L = tmen)	29
$[(\text{OC})_3\text{Tp}^*\text{MoCu}(\text{tmen})]$		29
$[(\text{OC})_3\text{Mo}(\mu\text{-C}_5\text{H}_4\text{PPh}_2)\text{Ag}]_2$	2.7467(4) ^a	36
$[(\text{OC})_3\text{M}(\mu\text{-C}_5\text{H}_4\text{PPh}_2)\text{M}']_2$ (M = Cr, Mo, W; M' = Ag, Au)	2.6579(8) ^a (M = Cr; M' = Ag) 2.7146(5) ^a (M = Mo; M' = Au) 2.7593(5) ^a (M = W; M' = Ag)	37
$[(\text{EtNC})\text{Cp}_2\text{MoAu}(\text{PPh}_3)]$		28
$[(\text{thf})_3\text{I}_2\text{LaRuCp}(\text{CO})_2]$		25
$[\text{Cp}^*\text{LaRuCp}(\text{CO})_2]$		25
$[(\text{thf})(\text{C}_5\text{H}_3\text{R}_2)\text{LuRuCp}(\text{CO})_2]$ (R = H, SiMe ₃)	2.955(2) (R = H)	25
$[\text{Cp}_3\text{UMCp}(\text{CO})_2]$ (M = Fe, Ru)		254

^a Unbridged distances.

the descriptions of the complexes: (i) the overall charge on the ligand; (ii) the denticity of the ligand, that is, the number of coordinative bonds which it forms with the metals; (iii) the number of atoms forming the bridge between the metal centers. It has also been necessary to extend the κ -nomenclature to specify which metal is coordinated by which donor atom. For example, the $\text{Ph}_2\text{PCH}_2\text{O}^-$ ligand in $[\text{Cp}^*\text{Zr}(\mu\text{-OCH}_2\text{PPh}_2)_2\text{RhMe}_2]$ is σ -bonded to zirconium through the oxygen and coordinated to the rhodium through the phosphorus,¹⁴ a behavior we have described as $\kappa_{\text{Zr}}\text{O}, \kappa_{\text{Rh}}\text{P}$.

A. Compounds with Unbridged Metal–Metal Bonds

Heterobimetallic compounds containing a metal–metal bond unbridged by other ligands (see Table 1) are particularly interesting for a number of reasons.¹⁵ The existence of a direct metal–metal interaction in these complexes is unquestionable, which allows an examination of its strength and reactivity without

complications arising from the reactivity of bridging ligands.

They are usually prepared by metathesis of a halide ligand with an organometallic anion. The most common reaction is the replacement of the halide ligand on a group 4 metal by an anionic complex such as $[\text{CpM}(\text{CO})_2]^-$ (M = Fe, Ru)^{16–21} or $[\text{M}(\text{CO})_4]^-$ (M = Co, Rh).^{17,18,22–24} A similar reaction has been used to prepare heterobimetallic lanthanide complexes.²⁵ However, the group 6 metals can also form organometallic anions $[\text{CpM}(\text{CO})_3]^-$ (M = Co, Mo, W), and these will displace halide ligands from complexes of group 9 metals.^{26,27} A nucleophilic molybdenum complex, $[\text{Cp}_2\text{Mo}(\text{CNet})]$, will displace chloride from $[(\text{Ph}_3\text{P})\text{AuCl}]$, forming the heterobimetallic complex $[\text{Cp}_2(\text{EtNC})\text{MoAu}(\text{PPh}_3)]^+$.²⁸ Similarly, the $[\text{tris}(\text{pyrazolyl})\text{borate}]$ molybdate anions $[\{\text{HB}(\text{C}_3\text{HR}_2\text{N}_2)_3\}\text{Mo}(\text{CO})_3]^-$ (R = H, Me) will displace a halide ligand from a copper(II) center, forming complexes such as $[(\text{OC})_3\text{TpMoCuL}]$ (L = PPh₃, tmen).²⁹

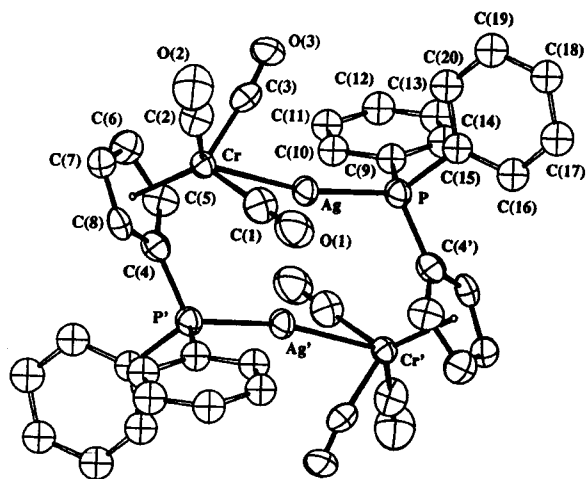


Figure 1. Crystal structure of $[(OC)_3Cr(\mu-C_5H_4PPh_2)Ag]_2$. Reprinted with permission from ref 36. Copyright 1998 Royal Society of Chemistry.

A second approach is the protonolysis of an early metal complex by an acidic "hydride" complex of a late metal: molecules which have been eliminated this way leading to metal–metal bonded complexes include toluene (from a benzyl ligand),²⁴ dimethylamine,^{30,31} and methane.²³

Direct addition of $[FeMe(CO)_4]^-$ to $[W(CO)_5(thf)]$ results in the heterobimetallic anion $[(OC)_5WFeMe(CO)_4]^-$, with the methyl group cis to the tungsten–iron bond.³²

A redistribution reaction between $[(OC)_2(C_5H_4R)W\equiv W(C_5H_4R)(CO)_2]$ ($R = Ac, CO_2Me$) and $[Co_2(CO)_8]$ gives the heterobimetallic complex $[(OC)_3(C_5H_4R)WCo(CO)_4]$ in 40–50% yield, along with other monometallic complexes.³³

Reaction of the triply bonded homobimetallic dimers $[MCp(CO)_2]_2$ ($M = Mo, W$) with $Co_2(CO)_8$ leads to the heterobimetallic complexes $[(OC)_3CpMCo(CO)_4]$ in yields of about 40%.³⁴ The X-ray crystal structure shows no fewer than five carbonyl ligands bent over the molybdenum–cobalt bond, but although two of them have asymmetry parameters³⁵ of slightly less than 0.6, they cannot truly be considered to be semibridging.

The cyclic tetranuclear complexes $[(OC)_3M(\mu-C_5H_4PPh_2)M']_2$ ($M = Cr, Mo; M' = Ag, Au$; see Figure 1) are formed on reaction of $[(C_5H_4PPh_2)M(CO)_3]^-$ with $AgBF_4$ or $[(Ph_3P)AuCl]$.^{36,37} The unbridged group 6–group 11 bond is relatively labile, as shown by the formation of the mixed species $[(OC)_3Mo(\mu-C_5H_4PPh_2)}_2AgAu]$ from $[(OC)_3Mo(\mu-C_5H_4PPh_2)Ag]_2$ and $[(OC)_3Mo(\mu-C_5H_4PPh_2)MAu]_2$, and by the double epimerization process seen in the silver complexes.³⁷

B. Compounds Containing Neutral Bridging Ligands

1. Diphosphine-Bridged Compounds

Substitution of the two chloro ligands in $[PdCl_2(dppm)]$ by $[CpM(CO)_3]^-$ ($M = Mo, W$) affords the trinuclear complex $[PdM_2Cp_2(CO)_5(dppm)]$, which contains a μ_3-CO ligand in addition to a dppm bridge between the palladium atom and one of the two early metal centers (Table 2). These compounds react with 1 equiv of dppm to give the cationic binuclear species $[(OC)CpM(\mu-CO)(\mu-dppm)_2Pd]^+$: the X-ray crystal structure of the molybdenum complex (Figure 2) shows that the carbonyl bridge is remarkably symmetrical.³⁸

Complexes in which dppm acts as a monodentate ligand have been used to prepare heterobimetallic complexes. Indeed, $[MoClCp(CO)_2(\eta^1-dppm)]$ undergoes a comproportionation reaction with $[Pt(C_2H_4)(PPh_3)_2]$ to give $[(OC)_2CpMo(\mu-dppm)PtCl(PPh_3)]$ (see Figure 3). Similarly, *fac*- $[Mo(CO)_3(bipy)(\eta^1-dppm)]$ reacts with $[RhCl(nbd)]_2$ to produce a compound formulated by the authors as $[(OC)_2(bipy)Mo(\mu-CO)(\mu-dppm)RhCl(CO)]$, although no justification was given for the origin of the fourth carbonyl ligand.³⁹ In our opinion, the bridging CO ligand is classical, as indicated by its stretching frequency of 1755 cm^{-1} . Further investigations on the reaction of $[RhCl(nbd)]_2$ and $[M(CO)_3L_2(\eta^1-dppm)]$ ($M = Mo, W; L_2 = phen, bipy$) led the authors to propose a tricarbonyl formulation with the diolefin ligand retained, $[(OC)_2L_2M(\mu-CO)(\mu-dppm)RhCl(nbd)]$.⁴⁰

The amino bis(phosphite) ligand $(iPrO)_2PNMeP(O^iPr)_2$ also forms complexes with molybdenum and

Table 2. Diphosphine-Bridged Heterobimetallic Compounds

	$r(M-M)/\text{\AA}$	ref
$[(OC)_2Mo(\mu-Cl)(\mu-CO)\{\mu-MeN(P[OMe]_2)_2\}_2M(CO)]$ ($M = Rh, Ir$)	2.858(1) ($M = Rh$) 2.888(1) ($M = Ir$)	41
$[(OC)_2Mo(\mu-CO)_2\{\mu-MeN(P[OMe]_2)_2\}_2RhCl]$		41
$[(OC)_3Mo\{\mu-MeN(PF_2)_2\}_2RhCl(PPh_3)]$		42
$[(OC)_3Mo\{\mu-MeN(PF_2)_2\}_2IrCl(CO)(PPh_3)]$		42
$[(OC)_2LM(\mu-CO)(\mu-dppm)RhCl(nbd)]$ ($M = Mo, W; L = bipy, phen$)		40
$[(OC)_3M(\mu-Cl)(\mu-CO)(\mu-dppm)Rh(nbd)]$ ($M = Mo, W$)		159
$[(OC)_2(phen)W(\mu-CO)(\mu-dppm)Rh(cod)]$		40
$[(OC)_2W(\mu-Cl)(\mu-CO)\{\mu-MeN(P[OMe]_2)_2\}Ir(CO)]$		41
$[(OC)_3Mo\{\mu-MeN(PF_2)_2\}_2M(PPh_3)]$ ($M = Ni, Pt$)	2.915(1) ($M = Pt$)	42
$[(OC)_3Mo(\mu-dppm)_2PtHCl]$		267
$[(OC)_3Mo(\mu-CO)(\mu-dppm)_2PtH]^+$		267
$\{[(OC)_3Cp_2M_2\}\{\mu_3-CO\}(\mu-dppm)Pd(CO)]$ ($M = Mo, W$)		38
$[(OC)CpM(\mu-CO)(\mu-dppm)_2Pd]^+$ ($M = Mo, W$)	2.799(1) ($M = Mo$)	38
$[(OC)_2CpM(\mu-dppm)PtCl(PPh_3)]$ ($M = Mo, W$)		38
$\{[(OC)_3Cp_2M_2\}\{\mu_3-CO\}(\mu-dppm)Pt(CO)]$ ($M = Mo, W$)		43
$[(OC)_2CpM(\mu-dppm)Pt(CO)MCp(CO)_3]$ ($M = Mo, W$)		43
$[(OC)_2CpM(\mu-dppm)Pt(dppm)]^+$ ($M = Mo, W$)		43
$[(OC)_3W(\mu-dppm)_2Pt(C\equiv CH)_2]$		149

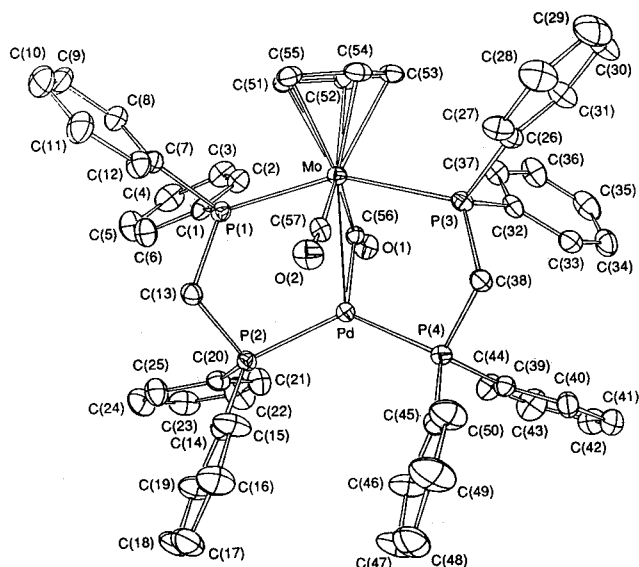


Figure 2. Crystal structure of $[(OC)CpMo(\mu-CO)(\mu-dppm)_2Pd]^+$. Reprinted with permission from ref 38. Copyright 1991 Royal Society of Chemistry.

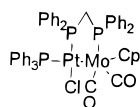


Figure 3. Proposed structure of the product of the reaction between $[CpMoCl(CO)_2(dppm)]$ and $[Pt(C_2H_4)(PPh_3)_2]$. Redrawn from ref 40.

tungsten in which it is monodentate, and these have been used to form heterobimetallic complexes with rhodium and iridium, $[(OC)_2M(\mu-Cl)(\mu-CO)\{\mu-MeN(P\{O^iPr\}_2)_2-P,P'\}_2M'(CO)]$ ($M = Mo, W; M' = Rh, Ir$). For the rhodium complexes, a minor isomer is also observed in which the bridging chloro ligand and the terminal carbonyl are interchanged.⁴¹

The ligand $MeN(PF_2)_2$ is also formally analogous to dppm, and forms similar bridges between two metal centers. Reaction of *fac*- $[Mo(CO)_3\{\eta^2-MeN(PF_2)_2\}\{\eta^1-MeN(PF_2)_2\}]$ with $[Ni(CO)_2(PPh_3)_2]$ or $[Pt(C_2Ph_2)(PPh_3)_2]$ affords the complexes $[(OC)_3Mo(\mu-F_2PNMePF_2)_2M(PPh_3)]$ ($M = Ni, Pt$), the X-ray crystal structure of the platinum complex of which has been determined. When the molybdenum precursor complex is reacted with $[MCl(CO)(PPh_3)_2]$ ($M = Rh, Ir$), the products are $[(OC)_3Mo(\mu-F_2PNMePF_2)_2RhCl(PPh_3)]$ and $[(OC)_3Mo(\mu-F_2PNMePF_2)_2IrCl(CO)(PPh_3)]$, respectively.⁴²

Reaction of $[PtCl_2(dppm)]$ with the carbonyl metalates $[MCp(CO)_3]^-$ ($M = Mo, W$) gives the trinuclear species $[(OC)CpM(\mu-dppm)\{\mu-MCp(CO)_2\}(\mu_3-CO)Pt(CO)]$. These react further with dppm to give binuclear complexes $[(OC)_2CpM(\mu-dppm)Pt(dppm)]^+$, which can be formed directly from the carbonyl metalates and $[Pt(dppm)_2]^{2+}$. Carbonylation of the trinuclear species leads to cleavage of the bond between the early metal centers, forming $[(OC)_2CpM(\mu-dppm)Pt(CO)MCp(CO)_3]$.⁴³

2. Carbonyl-Bridged Compounds

Bridging carbonyl ligands are extremely common in heterobimetallic complexes of the group 6 elements: Table 3 lists those which fall within the scope

of the current review. Mostly, these contain other bridging ligands apart from CO, and it has been convenient to discuss them in other sections.

Elimination of methane between group 6 metal hydrides and $[IrMe(CO)(PPh_3)_2]$ leads to the bis(carbonyl)-bridged complexes $[(OC)CpM(\mu-CO)_2Ir(PPh_3)_2]$ ($M = Mo, W$).⁴⁴ An analogous tungsten-rhodium complex has been formed by displacement of chloride from $[RhCl(PPh_3)_3]$ by the anionic complex $[WCp^*(CO)_3]^-$.⁴⁵ These compounds have very short metal-metal bonds of around 2.58 Å, with a classic bridging arrangement of the carbonyls. However, the related tungsten-copper species $[(OC)_2Cp^*WCu(PPh_3)]$ appears to have only weakly bridging carbonyls, considered by the authors to be semibridging.⁴⁵ The geometrical nonrigidity of these compounds has been studied by variable-temperature NMR spectroscopy.⁴⁶

The anionic molybdenum-copper complex $[\{Tp^*Mo(\mu-CO)_3\}_2Cu]^-$, formed by the reaction of $[Tp^*Mo(CO)_3]^-$ with CuI in the presence of dppe, contains semibridging carbonyl ligands⁴⁷ in contrast to similar complexes, e.g., $[(OC)_3TpMoCu(tmen)]$, in which the molybdenum-copper bond is unbridged.²⁹

Thermolytic decarbonylation (refluxing hexane) of $[(OC)_2CpM(\mu-CO)_2NiCp^*]$ ($M = Mo, W$) yields the triply bridged species $[CpM(\mu-CO)_3NiCp^*]$. The related compound $[Cp^*W(\mu-CO)_3NiCp^*]$ has been crystallographically characterized, and shows a remarkably short W-Ni distance of 2.475 Å.⁴⁸

3. Other Neutral Bridging Ligands

Yih and co-workers have reported the crystal structure of a tungsten-palladium complex with a bridging phosphino dithioformate ester, $[(OC)_5W\{\mu-Ph_2PC(=S)SMe-\kappa_W P, \kappa_{Pd} C=S\}Pd(PPh_3)_2]$ (see Figure 4). This complex results from the addition of $[Pd-$

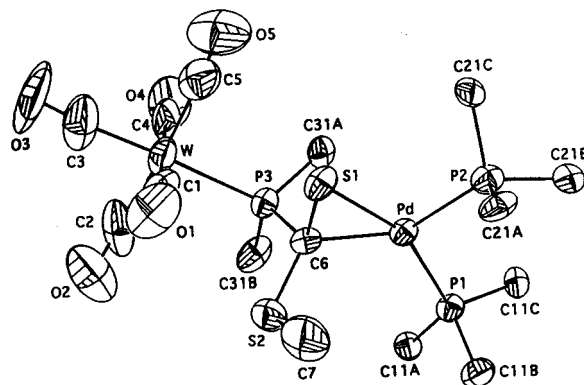


Figure 4. Crystal structure of $[(OC)_5W\{\mu-Ph_2PC(=S)SMe\}Pd(PPh_3)_2]$: phenyl rings are omitted for clarity. Reprinted with permission from ref 49. Copyright 1994 Elsevier Science Ltd.

$(PPh_3)_4]$ to $[W(CO)_5(Ph_2PCS_2Me)]$: it undergoes slow disproportionation at room temperature to give monometallic species.⁴⁹

In studying the electrophilic attack of various reagents on the nonbonded sulfur of the carbon disulfide ligand in $[(C_5H_4SiMe_3)_2NbCl(\eta^2-CS_2)]$, Antiñolo and co-workers have shown that a $M(PPh_3)_2$ group ($M = Cu, Ag, Au$) can attach itself at this site,

Table 3. Carbonyl-Bridged Heterobimetallic Compounds

	$r(M-M)/\text{\AA}$	ref
$[\text{Cp}_2\text{Nb}(\mu\text{-PR}_2)(\mu\text{-CO})\text{Fe}(\text{CO})_3]$ (R = Me, Ph)	2.884(2) (R = Ph)	83
$[\text{Cp}_2\text{Nb}(\mu\text{-PPhR})(\mu\text{-CO})\text{Fe}(\text{CO})_3]$ (R = H, Me)		84
$[(\text{OC})_2\text{CpW}(\mu\text{-PPh}_2)(\mu\text{-CO})\text{Fe}(\text{CO})_3]$	2.8308(22)	92
$[(\text{OC})_3\text{LW}(\mu\text{-PPh}_2)(\mu\text{-CO})\text{FeCp}(\text{CO})]$ (L = CO, PMe ₃ , P(OMe) ₃ , PPh ₂ , PPh ₃)	2.8548(11) (L = PPh ₃)	86
$[(\text{OC})_4\text{W}(\mu\text{-PPh}_2)(\mu\text{-CO})\text{FeCp}(\text{CO})]$	2.851(3)	88, 89
$[(\text{OC})_2\text{LM}(\mu\text{-CO})(\mu\text{-dppm})\text{RhCl}(\text{nbid})]$ (M = Mo, W; L = bipy, phen)		40
$[(\text{OC})_3\text{M}(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})\text{Rh}(\text{nbid})]$ (M = Mo, W)	2.945(4) (M = Mo)	159
$[(\text{OC})\text{CpM}(\mu\text{-CO})_2\text{Ir}(\text{PPh}_3)_2]$ (M = Mo, W)	2.579(1) (M = Mo)	44
	2.583(1) (M = W)	
$[\text{Cp}_2\text{Mo}(\mu\text{-H})(\mu\text{-CO})\text{Co}(\text{CO})_3]$	2.8449(4)	66
$[(\text{OC})_2\text{Mo}(\mu\text{-Cl})(\mu\text{-CO})\{\mu\text{-MeN}(\text{P}[\text{OMe}]_2)_2\}_2\text{M}(\text{CO})]$ (M = Rh, Ir)	2.858(1) (M = Rh)	41
	2.888(1) (M = Ir)	
$[(\text{OC})_2\text{Mo}(\mu\text{-CO})_2\{\mu\text{-MeN}(\text{P}[\text{OMe}]_2)_2\}_2\text{RhCl}]$		41
$[(\text{OC})_2(\text{phen})\text{W}(\mu\text{-CO})(\mu\text{-dppm})\text{RhCl}(\text{cod})]$		40
$[(\text{OC})(\text{C}_5\text{R}_5)\text{W}(\mu\text{-CO})_2\text{Rh}(\text{PPh}_3)_2]$ (R = H, Me)	2.5820(6) (R = Me)	45, 46
$[(\text{OC})_2\text{W}(\mu\text{-Cl})(\mu\text{-CO})\{\mu\text{-MeN}(\text{P}[\text{OMe}]_2)_2\}_2\text{Ir}(\text{CO})]$		41
$[(\text{OC})_4\text{M}(\mu\text{-PPh}_2)(\mu\text{-CO})\text{Pt}(\eta^3\text{-C}_3\text{H}_3)]$ (M = Cr, Mo, W)	2.820(1) (M = Cr)	101
$[(\text{BuNC})_2\text{CpMo}(\mu\text{-TolCC}_6\text{H}_4\text{CH}_2\text{NMe}_2)(\mu\text{-CO})\text{PdI}]$	2.692(2)	200
$[(\text{OC})\text{CpM}(\mu\text{-CO})_2\text{NiCp}^*]$ (M = Mo, W)	2.475(2), 2.457(2) ^a (M = W)	48
$[(\text{OC})_2\text{CpM}(\mu\text{-CH}_2)(\mu\text{-CO})\text{NiCp}^*]$ (M = Mo, W)	2.5689(6) (M = W)	202
$[(\text{OC})\text{Cp}^*\text{M}(\mu\text{-CH}_2\text{CMeCMe})(\mu\text{-CO})\text{NiCp}]$ (M = Mo, W)		212
$[(\text{OC})\text{CpM}(\mu\text{-RCC}_6\text{H}_4\text{CH}_2\text{Y})(\mu\text{-CO})\text{PdX}]$ (M = Mo, W; X = Cl, I; R = Tol, C ₅ H ₇ , C ₆ H ₄ tBu, C ₆ H ₃ Me ₂ ; Y = NMe ₂ , SMe, C ₅ H ₄ N)		199
$[(\text{OC})\text{CpM}(\mu\text{-TolCC}_6\text{H}_4\text{CC}_6\text{H}_4\text{Y})(\mu\text{-CO})\text{PdCl}]$ (M = Mo, W; Y = NMe ₂ , SMe)	2.6973(3) (M = W; Y = SMe)	199
$[(\text{OC})_3\text{Cp}_2\text{M}_2\{\mu_3\text{-CO}(\mu\text{-dppm})\text{M}'(\text{CO})\}]$ (M = Mo, W; M' = Pd, Pt)		38, 43
$[(\text{OC})\text{CpM}(\mu\text{-CO})(\mu\text{-dppm})_2\text{Pd}]^+$ (M = Mo, W)	2.799(1) (M = Mo)	38
$[(\text{Et}_3\text{P})(\text{OC})_3\text{M}(\mu\text{-PPh}_2)(\mu\text{-CO})\text{PtH}(\text{PCy}_3)]$ (M = Mo, W)		101
$[(\text{OC})(\text{PhS})\text{Cp}^*\text{Mo}(\mu\text{-SPh})(\mu\text{-CO})\text{NiCp}^*]$		75
$[(\text{OC})_3\text{Mo}(\mu\text{-CO})(\mu\text{-dppm})_2\text{PtH}]^+$		267
$[(\text{OC})_2\text{Cp}^*\text{W}(\mu\text{-CO})(\mu\text{-SO}_2)\text{NiCp}^*]$	2.6523(6)	65
$[(\text{OC})\text{CpW}(\mu\text{-CO})_2\text{NiCp}^*(\text{CO})]$		266
$[(\text{OC})\text{CpW}(\mu\text{-CO})(\mu\text{-PhC}\equiv\text{CH})\text{NiCp}^*]$		266
$[(\text{OC})(\text{RE})\text{Cp}^*\text{W}(\mu\text{-ER})(\mu\text{-CO})\text{NiCp}^*]$ (E = S; R = Me, Ph. E = Se; R = Ph)	2.602(1) (E = S; R = Ph)	75
$[\text{Cp}(\text{O}=\text{W})(\mu\text{-TolCC}_6\text{H}_4\text{CH}_2\text{NMe}_2)(\mu\text{-CO})\text{PdCl}]$	2.6939(6)	201
$[(\text{OC})_2\text{CpW}(\mu\text{-PCy}_2)(\mu\text{-CO})\text{PtH}(\text{PCy}_2\text{H})]$		99
$[(\text{C}_5\text{R}_5)\text{M}(\mu\text{-CO})_3\text{Cu}(\text{PPh}_3)]$ (M = Mo, W; R = H, Me)		45, 46
$[\{\text{Tp}^*\text{Mo}(\mu\text{-CO})_3\}_2\text{Cu}]^-$	2.5493(6)	47

^a Two independent molecules per unit cell.

forming a bimetallic complex in which the two metal centers are held relatively distant from one another.⁵⁰

Reaction of the tricarbonylchromium-substituted diphosphine ligand $[\text{Cr}(\text{CO})_3\{\eta^6\text{-C}_6\text{H}_5\text{CH}_2\text{P}(\text{Ph})\text{CH}_2\text{-CH}_2\text{CH}_2\text{PPh}_2\}]$ with $[\text{PtMe}_2(\text{cod})]$ leads to the heterobimetallic complex $[(\text{OC})_3\text{Cr}\{\mu\text{-C}_6\text{H}_5\text{CH}_2\text{P}(\text{Ph})\text{CH}_2\text{-CH}_2\text{CH}_2\text{PPh}_2\text{-}\kappa_{\text{Cr}}, \text{Ph}, \kappa_{\text{Pt}}, \text{P}, \kappa_{\text{Pt}}, \text{P}'\}\text{PtMe}_2]$. The X-ray crystal structure (Figure 5) shows that the two metal centers are far-separated from one another (5.658 Å).⁵¹

The coordination polymer $[(\text{OC})_2\text{LCr}(\mu\text{-Ph}_2\text{PC}_6\text{H}_4\text{-PPh}_2\text{-}\kappa_{\text{Cr}}, \text{C}_6\text{H}_4, \kappa_{\text{Rh}}, \text{P}, \kappa_{\text{Rh}}, \text{P}')\text{RhCl}(\text{CO})]_n$ (L = CO, PBus₃; see Figure 6) has been prepared by reacting the chromium η^6 -diphosphine complex with $[\text{RhCl}(\text{CO})_2]_2$.⁵²

Reaction of the organometallic anion $[(\eta^5\text{-C}_5\text{H}_4\text{R})\text{M}(\text{CO})_3]^-$ (M = Mo, W; R = Ac, CO₂Me) with $[\text{Co}_2(\text{CO})_6(\mu\text{-PhC}\equiv\text{CPh})]$ leads to substitution of one of the Co(CO)₃ groups by the early metal center. The molybdenum complex has been crystallographically characterized, and shows a Mo–Co distance of 2.687 Å.⁵³

An N₂P₂ tetradentate ligand has been prepared by addition of the N–H bond of a diamine to the C=C double bond of coordinated bis(diphenylphosphino)ethene. Heterobimetallic complexes of the type $[(\text{OC})_4\text{M}\{\mu\text{-}(\text{Ph}_2\text{P})_2\text{CHCH}_2\text{N}(\text{CH}_2)_3\text{NMe}_2\text{-}\kappa_{\text{M}}, \text{P}, \kappa_{\text{M}}, \text{P}', \kappa_{\text{M}}, \text{N}, \kappa_{\text{M}}, \text{N}'\}\text{M}'(\text{OAc})_2]$ (M = Cr, Mo; M' = Ni, Cu) have been prepared, and the X-ray crystal structure of the chromium–copper complex has been determined (see Figure 7).⁵⁴

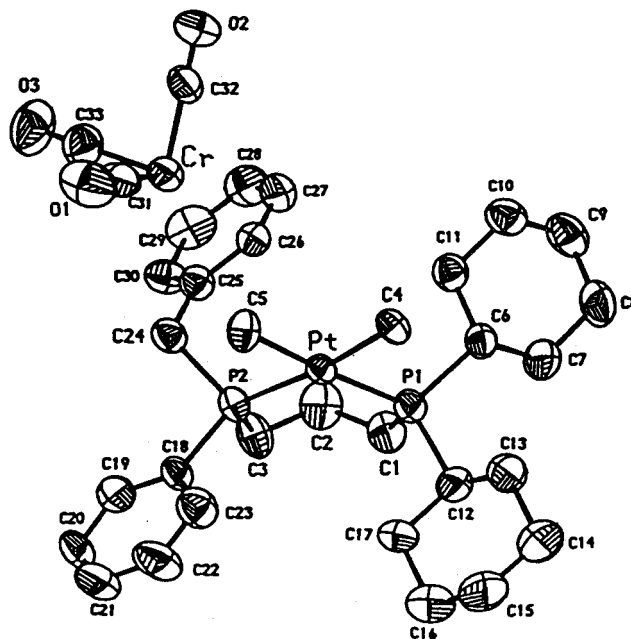


Figure 5. Crystal structure of $[(\text{OC})_3\text{Cr}\{\mu\text{-C}_6\text{H}_5\text{CH}_2\text{PPhCH}_2\text{-CH}_2\text{CH}_2\text{PPh}_2\}\text{PtMe}_2]$. Reprinted with permission from ref 51. Copyright 1991 Elsevier Science Ltd.

Reaction of the triphosphoxane rings $(\text{R}_2\text{NPO})_3$ (R = Cy, ⁱPr) with $[\text{Fe}_2(\text{CO})_9]$ or $[\text{MCl}_2(\text{nbid})]$ (M = Ni, Pd) leads to a ring expansion, giving complexes of the tetraphosphoxane systems. These retain phos-

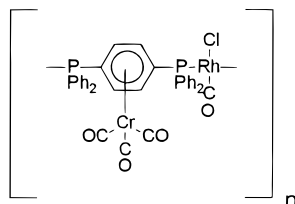


Figure 6. Proposed structure of the polymeric product of the reaction of $[\text{Cr}(\eta^6\text{-Ph}_2\text{PC}_6\text{H}_4\text{PPh}_2)(\text{CO})_3]$ with $[\text{RhCl}(\text{CO})_2]_2$. Redrawn from ref 52.

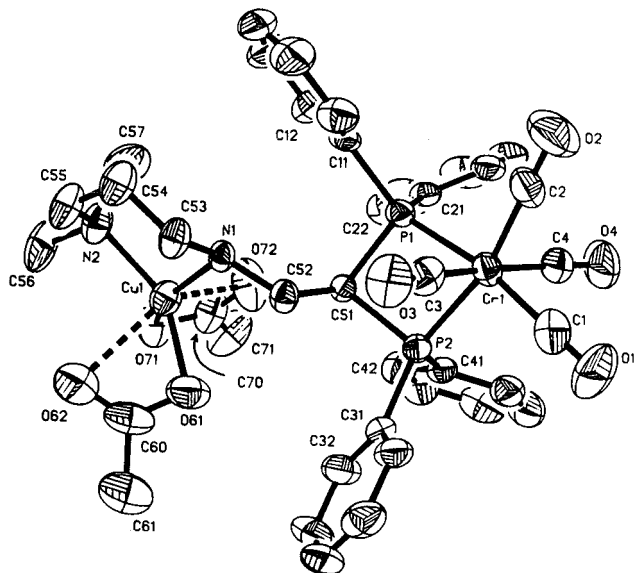


Figure 7. Crystal structure of $[(\text{OC})_4\text{Cr}\{\mu\text{-(Ph}_2\text{P)}_2\text{CH-CH}_2\text{N}(\text{CH}_2)_3\text{NMe}_2\}\text{Cu}(\text{OAc})_2]$. Reprinted with permission from ref 54. Copyright 1993 Wiley-VCH Verlag GmbH.

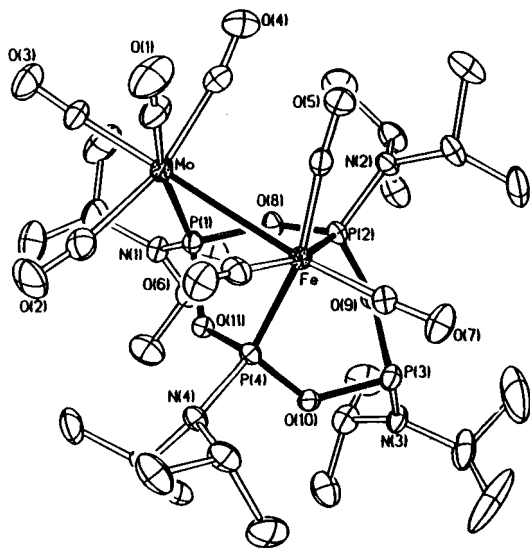


Figure 8. Crystal structure of $[(\text{OC})_4\text{Mo}\{\mu\text{-(}^i\text{PrNPO)}_4\}\text{Fe}(\text{CO})_3]$. Reprinted from ref 55. Copyright 1995 American Chemical Society.

phorus centers which can bind one or two other metals. The crystal structure of the molybdenum-iron complex $[(\text{OC})_4\text{Mo}\{\mu\text{-(}^i\text{Pr}_2\text{NPO)}_4\text{-}\kappa_{\text{Mo}}P, \kappa_{\text{Mo}}P', \kappa_{\text{Fe}}P', \kappa_{\text{Fe}}P''\}\text{Fe}(\text{CO})_3]$ (see Figure 8) shows that the two metal centers are positioned so as to complete the pseudoctahedral coordination of the other, despite the relatively long Mo-Fe distance of 3.034 Å.⁵⁵ The metallodiphosphine ligand $[(\text{OC})_4\text{Mo}\{\text{}^i\text{Pr}_2\text{-}$

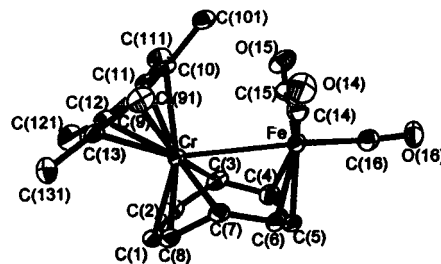


Figure 9. Crystal structure of $[\text{Cp}^*\text{Cr}(\mu\text{-cot})\text{Fe}(\text{CO})_3]$. Reprinted with permission from ref 61. Copyright 1997 Wiley-VCH Verlag GmbH.

$\text{NPO)}_4\}$ has been prepared, and reacted with a wide range of late metal precursors to give $[(\text{OC})_4\text{Mo}\{\mu\text{-(}^i\text{Pr}_2\text{NPO)}_4\text{-}\kappa_{\text{Mo}}P, \kappa_{\text{Mo}}P', \kappa_{\text{M}}P', \kappa_{\text{M}}P''\}\text{M}'\text{L}_n]$ ($\text{M}'\text{L}_n = \text{Fe}(\text{CO})_3, \text{NiBr}_2, \text{PdBr}_2, \text{PtCl}_2, \text{Cu}(\text{NCMe})_2^+, \text{Ag}(\text{NO}_3)$). The X-ray crystal structure of the molybdenum-nickel complex has been determined.^{56,57}

The binucleating bipyridyl type ligands bis(pyridyl)pyrazine and bis(pyridyl)quinoxaline have been used to prepare molybdenum-cobalt and molybdenum-nickel complexes $[(\text{OC})_3\text{LMo}(\mu\text{-L})\text{M}(\text{hfacac})_2]$ ($\text{L} = \text{CO}, \text{PPh}_3; \text{M} = \text{Co}, \text{Ni}$).^{58,59}

Complexes of the zwitterionic phosphanidene dithioformate ligand $^+\text{R}_3\text{P-CS}_2^-$, $[\text{MBr}(\eta^3\text{-C}_3\text{H}_5)(\text{S}_2\text{CPR}_3)(\text{CO})_2]$ ($\text{M} = \text{Mo}, \text{W}; \text{R} = \text{Cy}, ^i\text{Pr}$), react with $\text{Co}_2(\text{CO})_8$ to give the heterobimetallic complexes $[(\text{OC})_2(\eta^3\text{-C}_3\text{H}_5)\text{M}(\mu\text{-S}_2\text{CPR}_3)\text{Co}(\text{CO})_2]$, in which the cobalt atom is coordinated by a pair of electrons from one of the sulfur atoms and in an η^2 -manner by the double bond between the carbon and the other sulfur. The crystal structure of the molybdenum-cobalt complex ($\text{R} = \text{Cy}$) has been determined.⁶⁰

Reaction of the chromium cyclooctatetraene complexes $[(\text{C}_5\text{R}_5)\text{Cr}(\eta^6\text{-cot})]$ ($\text{R} = \text{H}, \text{Me}; \text{cot} = \text{cyclooctatetraene}$) with $[\text{Fe}(\text{CO})_3(\text{con})_2]$ ($\text{con} = \text{cyclooctene}$) results in the paramagnetic (33 electron) complexes $[(\text{C}_5\text{R}_5)\text{Cr}(\mu\text{-}\eta_{\text{Cr}}^5, \eta_{\text{Fe}}^3\text{-cot})\text{Fe}(\text{CO})_3]$. Only the synfacial products were formed, as shown by the X-ray crystal structure of the $\text{R} = \text{Me}$ complex (Figure 9). The carbonyl ligand trans to chromium is readily substituted by PR'_3 , and the $\text{R} = \text{H}, \text{PR}'_3 = \text{PMe}_3$ and $\text{R} = \text{Me}, \text{PR}'_3 = \text{P}(\text{OEt})_3$ complexes have been crystallographically characterized. The chromium-iron distances are around 3.0 Å in all these complexes. Solid solution EPR spectra are consistent with the unpaired electron residing primarily on the chromium center in a d_z^2 -type orbital ($g_{\text{iso}} = 1.991\text{--}1.995, a^{53}\text{Cr} = 18.9\text{--}19.0 \text{ G}$): hyperfine coupling to the hydrogens of the η^5 -cyclooctatetraene ligand ($a(^1\text{H}) = 3.2\text{--}5.4 \text{ G}$) and to the phosphorus center (when present, $a(^{31}\text{P}) = 13.3\text{--}34.2 \text{ G}$) is also observed (see section IV.B).⁶¹

The cyclodiphosphazane ligand $(\text{RO})\text{P}(\text{NPh})_2\text{P}(\text{OR})$ ($\text{R} = \text{Tol}, \text{CH}_2\text{CF}_3$) binds to molybdenum(0) or tungsten(0) centers through one of the phosphorus atoms only, leaving the other free to bind a second metal center. In this way, the complexes $[(\text{OC})_4\text{Mo}\{\mu\text{-(MeC}_6\text{H}_4\text{O})\text{P}(\text{NPh})_2\text{P}(\text{OC}_6\text{H}_4\text{Me})\text{-}\kappa_{\text{Mo}}P, \kappa_{\text{M}}P'\}_2\text{M}'\text{Cl}_2]$ ($\text{M}' = \text{Pd}, \text{Pt}$; see Figure 10) and $[(\text{OC})_4\text{LM}\{\mu\text{-(MeC}_6\text{H}_4\text{O})\text{P}(\text{NPh})_2\text{P}(\text{OC}_6\text{H}_4\text{Me})\text{-}\kappa_{\text{M}}P, \kappa_{\text{M}}P'\}_2\text{M}'\text{Cl}_2]$ ($\text{M} = \text{Mo}; \text{L} = \text{P}(\text{OMe})_3; \text{M} = \text{W}, \text{L} = \text{HNC}_5\text{H}_{10}$) have been prepared.⁶²

The unbridged heterobimetallic compound $[(\text{OC})_2\text{-}(\text{Ph}_3\text{P})\text{CpMoCo}(\text{CO})_3(\text{PPh}_3)]$ reacts with alkynes $\text{PhC}\equiv$

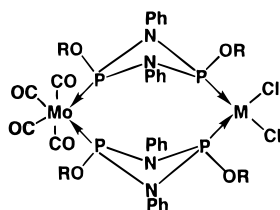


Figure 10. Proposed structure of $[(OC)_4Mo\{\mu-(MeC_6H_4O)P-(NPh)_2P(OC_6H_4Me)\}_2MCl_2]$ ($M = Pd, Pt$). Redrawn from ref 62.

CR ($R = H, Ph, SiMe_3$) to give alkyne-bridged complexes $[(OC)_2CpMo(\mu-PhC\equiv CR)Co(CO)_2L]$ ($L = CO, PPh_3$). When $R = H$ and $SiMe_3$, the reaction can continue to give “flyover” complexes (see section III.D.7).^{63,64}

Reaction of sulfur dioxide with $[Cp^*W(\mu-CO)_3NiCp^*]$ leads to incorporation of the SO_2 in a bridging position, as shown by X-ray diffraction studies of the product, $[(OC)_2Cp^*W(\mu-SO_2)(\mu-CO)NiCp^*]$.⁶⁵

C. Compounds Containing Monoanionic Bridging Ligands

1. Hydrido-Bridged Compounds

Several $[(C_5H_4SiMe_3)NbH\{P(OR)_3\}]$ ($R = Me, Et, Ph$) complexes have been prepared. The $(Ph_3P)Au^+$ cationic species appears to react with the niobium hydride bond, giving rise to a $Nb(\mu-H)Au$ framework.⁵⁰

The acidity of $[HCo(CO)_4]$ allows it to protonate the coordinated carbon dioxide of $[Cp_2Mo(\eta^2-CO_2)]$, producing the charge-separated bimetallic compound $[Cp_2MoH(CO)]^+[Co(CO)_4]^-$, which slowly loses carbon monoxide to give the bridged species $[Cp_2Mo(\mu-H)(\mu-CO)Co(CO)_3]$. The $Mo-Co$ distance is 2.845 Å; calculations at the extended Hückel level indicate only a weak bonding interaction (see section IV.C).⁶⁶

The electrophilic “bent sandwich” compound $[Cp^*_2Yb]$ is able to react directly with the hydride or methyl ligands of $[PtX_2(dippe)]$ ($X = H, Me$; $dippe =$

$^iPr_2PCH_2CH_2P^iPr_2$), producing bishydrido, bismethyl, or mixed bridged complexes.⁶⁷ Other heterobimetallic complexes containing bridging hydride ligands are listed in Table 4.

2. Thiolato-Bridged and Related Bridged Compounds

The bridging properties of thiolato ligands in homobimetallic complexes are well-known, and they have also been widely used in heterobimetallic systems (see Table 5).

Thus, reaction of $[Cp_2Ti(SMe)_2]$ with 1/2 equiv of $[Ni(cod)_2]$ results in the trinuclear complex $[Ni\{\mu-SMe)_2TiCp_2\}_2]$.⁶⁸ This complex has been crystallographically characterized (see Figure 11) and shown to have a $Ti-Ni$ distance of 2.786 Å. The monosubstitution product $[Cp_2Ti(\mu-SMe)_2Ni(cod)]$ cannot be observed directly, but can be trapped by reaction with tricyclohexylphosphine to give $[Cp_2Ti(\mu-SMe)_2Ni(PCy_3)]$.⁶⁸ Similar complexes with selenolato and tellurolato bridges have also been prepared by reacting $[Cp_2Ti(EAr)_2]$ ($E = Se, Te$) with $[MCl_2(PhCN)_2]$ and $[M(dppe)_2]^{2+}$ ($M = Ni, Pd, Pt$): the binuclear complexes $[Cp_2Ti(\mu-EAr)_2MCl_2]$ and $[Cp_2Ti(\mu-EAr)_2M(dppe)]^{2+}$ were obtained and characterized by multinuclear NMR.⁶⁹

In some systems, the reaction proceeds with complete transfer of the thiolate ligands from the early metal to the late metal. Hence, $[Cp_2Ti(SR)_2]$ reacts with $[PtCl_2(cod)]$ to give insoluble platinum thiolates and $[Cp_2TiCl_2]$. It has been possible to isolate heterobimetallic species when R is an aryl group (phenyl or tolyl), and these have been formulated as $[Cp_2Ti(\mu-SR)_2PtCl(cod)]Cl$ or $[Cp_2Ti(\mu-Cl)(\mu-SR)PtCl(cod)]$ from solid-state ^{13}C NMR. However, these complexes decompose on dissolution, with thiolate transfer to platinum.⁷⁰ This transfer phenomenon has also been observed between $[Cp_2V(SMe)_2]$ and $[Ni(cod)_2]$, where redox processes are also involved.⁶⁸

The labile THF complexes $[M(C_6F_5)_2(thf)_2]$ ($M = Pd, Pt$) have been shown to be useful precursors for the formation of heterobimetallic complexes. Indeed,

Table 4. Hydrido-Bridged Heterobimetallic Compounds^a

	$r(M-M)/\text{Å}$	ref
$[XZr(\mu-Cl)(\mu-H)(\mu-C_5Me_4PMe_2)_2RuH(PPh_3)]$ ($X = Cl, H$)	3.130(1) ($X = Cl$)	107, 120
$[ClZr(\mu-H)_2(\mu-C_5Me_4PMe_2)_2RuX(PPh_3)]$ ($X = Cl, H$)		107
$[XCp_2Zr(\mu-N^tBu)(\mu-H)IrCp^*]$	2.977(1) ($X = NHTol$)	179, 180
($X = H, NHTol, OR, SiHMePh; R = ^tBu, Tol, CMe=CH_2$)	3.020(1) ($X = OTol$)	
$[XCp_2Zr(\mu-N^tBu)(\mu-H)IrCp^*]$ ($X = H, OCHO$)	nr ($X = OCHO$)	8
$\{[(RO)_3P](C_5H_4SiMe_3)_2Nb(\mu-H)Au(PPh_3)]$ ($R = Me, Et, Ph$)		50
$[Cp_2Mo(\mu-H)(\mu-CO)Co(CO)_3]$	2.8449(4)	66
$[(OC)_3Mo(\mu-CHCMeCHCMeCH)(\mu-H)Ir(PMe_3)(PEt_3)_2]$	2.854(2)	226
$[(OC)_5W(\mu-H)(\mu-SC_6H_4Et)Rh\{Ph_2PCH_2\}_3CH\}]$	3.0554(13)	73
$[(OC)_2CpMo(\mu-H)(\mu-PR_2)Pt(C_4H_6O)L]^+$ ($R = Ph, Cy; L = PCy_3, PPh_3$)	3.063(1) ($R = Ph; L = PCy_3$)	104
$[(OC)_2CpMo(\mu-H)(\mu-PCy(C_4H_7O))Pt(PPh_3)_2]^+$		104
$[(OC)(\eta^7-C_7H_7)Mo(\mu-H)(\mu-PCy_2)Pt(PPh_3)_2]^+$		103
$[(OC)_2CpMo(\mu-H)(\mu-PPh_2)PtL(PPh_3)]^+$ ($L = CO, MeCN$)		103, 267
$[(OC)_4M(\mu-H)(\mu-PR_2)Pt(PPh_3)_2]$ ($M = Cr, Mo, W; R = Ph, ^nPr$)		101
$[(OC)_4M(\mu-H)(\mu-PPh_2)PtL_2]$ ($M = Cr, Mo, W; L = PEt_3, PMe_2Ph$)	2.905(2) ($M = Cr; L = PEt_3$)	101
$[(OC)_4M(\mu-H)(\mu-PPh_2)Pt(CO)(PCy_3)]$ ($M = Cr, Mo, W$)		101
$[(OC)_2CpM(\mu-H)(\mu-PPh_2)Pt(PPh_3)_2]^+$ ($M = Mo, W$)		103
$[(OC)_2CpM(\mu-H)(\mu-PPh_2)PtCl(PPh_3)]$ ($M = Mo, W$)		103, 267
$[(OC)_2CpW(\mu-H)(\mu-PCy_2)Pt(CO)(PCy_2H)]^+$		99
$[(OC)_2CpW(\mu-H)(\mu-PCy_2)PtCl(PCy_2H)]$		99
$[Cp^*_2Yb(\mu-CH_3)(\mu-H)Pt(dippe)]$	3.388(9)	67

^a nr = not reported.

Table 5. Thiolato-Bridged Heterobimetallic Compounds^a

	$r(M-M)/\text{\AA}$	ref
[Cp ₂ Ti(<i>μ</i> -SPh) ₂ RuCp* ⁺ X] (X = Cl, H)	nr (X = Cl)	77
[Cp ₂ Ti(<i>μ</i> -SPh) ₂ RuCp* ⁺ L] ⁺ (L = MeCN, ^t BuCN)	nr (L = ^t BuCN)	77
[Cp ₂ Ti(<i>μ</i> -SCH ₂ CH ₂ CH ₂ S) ₂ Rh] _n		225
[CpTi(<i>μ</i> -SCH ₂ CH ₂ CH ₂ S) ₂ Rh(nbd)]	2.915(2)	225
[Cp ₂ Ti(<i>μ</i> -SCH ₂ CH ₂ CH ₂ PPh ₂) ₂ Ni]	2.852(3)	142
[Cp ₂ Ti(<i>μ</i> -SMe) ₂ Ni]	2.786(1)	74
[Cp ₂ Ti(<i>μ</i> -SMe) ₂ Ni(PCy ₃)]		74
[Cp ₂ Ti(<i>μ</i> -EC ₆ H ₅ R) ₂ M(dppe)] ²⁺ (E = Se, Te; R = H, Me, OMe, OEt; M = Ni, Pt)		69
[(C ₅ H ₄ R ₂ Ti(<i>μ</i> -SC ₆ F ₅) ₂ M(C ₆ F ₅) ₂) (R = H, SiMe ₃ ; R = H, F; M = Pd, Pt)	3.140(3) (R = SiMe ₃ ; R = H; M = Pd)	71
[Cp ₂ Ti(<i>μ</i> -TePh) ₂ MCl ₂] (M = Pd, Pt)		69
[Cp ₂ Ti(<i>μ</i> -SAr) ₂ PtCl ₂ (cod)] (Ar = Ph, Tol)		70
[Cp ₂ Zr(<i>μ</i> -SCH ₂ CH ₂ S) ₂ Ni(dppe)]		253
[{Cp ₂ Zr(<i>μ</i> -SCH ₂ CH ₂ S) ₂ ZrCp ₂ }M] (M = Ni, Pd)	2.866(1) (M = Pd)	253
[Cp ₂ Ti(<i>μ</i> -SCH ₂ CH ₂ S) ₂ Cu] _n		225
[CpTi(<i>μ</i> -SCH ₂ CH ₂ CH ₂ S) ₂ Cu] _n		225
[CpTi(<i>μ</i> -SCH ₂ CH ₂ S) ₂ Cu(PMe ₃)]	2.720(1)	225
[CpTi(<i>μ</i> -SCH ₂ CH ₂ CH ₂ S) ₂ Cu(PMe ₃)]		225
[Cp ₂ Ti(<i>μ</i> -SMe) ₂ Cu(PCy ₃)] ⁺		68
[Cp ₂ Ti(<i>μ</i> -SR) ₂ Cu(MeCN) ₂] ⁺ (R = Me, Et)	2.847(2) (R = Me)	68
[{Cp ₂ Ti(<i>μ</i> -SMe) ₂ } ₂ Cu] ⁺		68
[{Cp ₂ Ti(<i>μ</i> -SCH ₂ CH ₂ S) ₂ TiCp ₂ }Cu] ⁺		249
[Cp ₂ Ti{ <i>μ</i> -(SCH ₂ CH ₂ SCH ₂) ₂ CH ₂ }Cu] ⁺	2.832(3)	250
[Cp ₂ Ti(<i>μ</i> -SCH ₂ CH ₂ SEt) ₂ Cu] ⁺		250
[Cp ₂ Ti{ <i>μ</i> -(SCH ₂ CH ₂ SCH ₂) ₂ CH ₂ }Cu] ⁺		250
[{Cp ₂ Ti(<i>μ</i> -SCH ₂ CH ₂ CH ₂ S) ₂ TiCp ₂ }Ag] ⁺	3.246(7), 3.207(7) 3.279(6), 3.264(6) ^b	249
[{Cp ₂ Zr(<i>μ</i> -SCH ₂ CH ₂ S) ₂ ZrCp ₂ }Ag] ⁺	3.047(2), 3.058(2)	252
[{Cp ₂ Zr(<i>μ</i> -SCH ₂ CH ₂ CH ₂ S) ₂ ZrCp ₂ }Ag] ⁺	3.333(3), 3.280(3)	251, 252
[Cp ₂ V(<i>μ</i> -SEt) ₂ CuL] ⁺ (L = PPh ₃ , PCy ₃)		68
[Cp ₂ V(<i>μ</i> -SR) ₂ Cu(MeCN) ₂] ⁺ (R = Me, Et)		68
[{(OC) ₄ Mo(<i>μ</i> -Ph ₂ PC ₅ H ₄) ₂ }Ti(<i>μ</i> -SPh) ₂ M(C ₆ F ₅) ₂] (M = Pd, Pt)	3.014(1)	72
[(OC) ₅ W(<i>μ</i> -SC ₆ H ₄ CH=CH ₂)Rh{(Ph ₂ PCH ₂) ₃ CH}]		73
[(OC) ₅ W(<i>μ</i> -H)(<i>μ</i> -SC ₆ H ₄ Et)Rh{(Ph ₂ PCH ₂) ₃ CH}]	3.0554(14)	73
[(OC)(PhS)Cp*Mo(<i>μ</i> -SPh)(<i>μ</i> -CO)NiCp*]		75
[(OC)(RE)Cp*W(<i>μ</i> -ER)(<i>μ</i> -CO)NiCp*] (E = S; R = Me, Ph. E = Se; R = Ph)	2.602(1) (E = S; R = Ph)	75
[U{(<i>μ</i> -SPh) ₃ Cu(PPh ₃) ₂ }]	3.05(1)	76

^a nr = not reported. ^b Two independent molecules per unit cell.

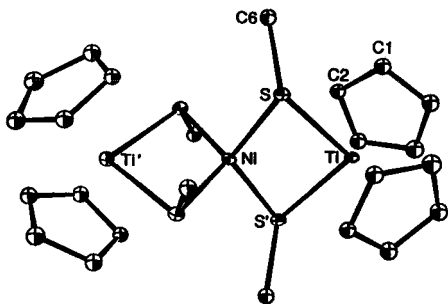


Figure 11. Crystal structure of $[\{Cp_2Ti(\mu-SMe)_2\}_2Ni]$. Reprinted from ref 68. Copyright 1989 American Chemical Society.

$[(C_5H_4R)_2Ti(SAr)_2]$ (R = H, SiMe₃; Ar = Ph, C₆F₅) reacts with *cis*-[M(C₆H₅)₂(thf)₂] to form the binuclear complexes $[(C_5H_4R)_2Ti(\mu-SAr)_2M(C_6F_5)_2]$. The palladium complex has been crystallographically characterized, and the structure shows no evidence of any Ti–Pd interaction.⁷¹ In a related reaction, $[(OC)_4Mo(\mu-Ph_2PC_5H_4)_2Ti(SPh)_2]$ reacts with $[M(C_6F_5)_2(thf)_2]$ to give the trimetallic species $[(OC)_4Mo(\mu-Ph_2PC_5H_4)_2Ti(\mu-SPh)_2M(C_6F_5)_2]$ (M = Pd, Pt). The X-ray structure of the platinum complex shows a Ti–Pt distance of 3.014 Å.⁷² The coordination of the molybdenum to the (diphenylphosphino)cyclopentadienyl ligands does not appear to have any effect on the TiS₂Pt core.

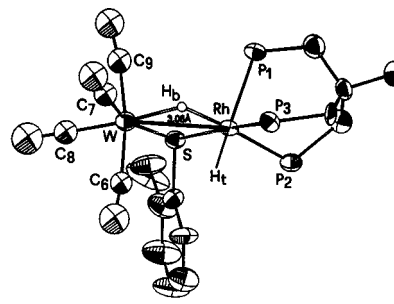


Figure 12. Crystal structure of $[(OC)_4W(\mu-H)(\mu-SC_6H_4Et)-RhH\{(Ph_2PCH_2)_3CH\}]$. Reprinted from ref 73. Copyright 1997 American Chemical Society.

The complex $[(OC)_4W(\mu-H)(\mu-SC_6H_4Et)RhH\{(Ph_2PCH_2)_3CH\}]$ has been prepared by the hydrogenation of $[(OC)_5W(\mu-SC_6H_4CH=CH_2-\kappa_W S, \kappa_{Rh} S, \kappa_{Rh} CH=CH_2)-Rh(triphos)]$ (see section V.G). The X-ray crystal structure (Figure 12) shows a W–Rh distance of 3.06 Å and an angle at the bridging sulfur of 77.1°.⁷³

The complex $[Cp_2Ti(SMe)_2]$ reacts with the cationic copper complex $[Cu(NCMe)_4]^+$ to give $[Cp_2Ti(\mu-SMe)_2Cu(NCMe)_2]^+$. The X-ray crystal structure shows a Ti–Cu distance of 2.847 Å.⁷⁴ The acetonitrile ligands are easily replaced by tricyclohexylphosphine or by another $Cp_2Ti(SMe)_2$ group, and in this manner $[Cp_2Ti(\mu-SMe)_2Cu(PCy_3)]^+$ and $[\{Cp_2Ti(\mu-SMe)_2\}_2Cu]^+$

Table 6. Phosphido-Bridged Heterobimetallic Compounds

	$r(M-M')/\text{\AA}$	ref
$[\text{Cp}_2\text{Zr}(\mu\text{-PPh}_2)_2\text{RhH}(\text{CO})\text{L}]$ (L = PPh ₃ , PEt ₃ , PCy ₃ , CO)	2.980(1) (L = PPh ₃)	80
$[\text{Cp}_2\text{M}(\mu\text{-PR}_2)\text{RhH}(\text{CO})(\text{PPh}_3)]$ (M = Zr, Hf; R = Ph, Cy)	2.964(1) (M = Hf; R = Ph)	80
$[(\text{C}_5\text{H}_4\text{SiMe}_3)_2\text{Zr}(\mu\text{-PPh}_2)_2\{\text{Rh}_2(\text{S}^i\text{Bu})_2(\text{CO})_2\}]$		79
$[\text{Cp}_2\text{M}(\mu\text{-PPh}_2)\text{IrH}(\text{CO})(\text{PPh}_3)]$ (M = Zr, Hf; R = Ph, M' = Rh, Ir. R = Cy; M' = Rh)		80
$[\{\text{Cp}_2\text{M}(\mu\text{-PEt}_2)_2\text{M}'\}]$ (M = Zr, Hf; M' = Ni, Pd, Pt)		82
$[\text{Cp}_2\text{Ti}(\mu\text{-C}\equiv\text{CPh})(\mu\text{-PPh}_2)\text{Ni}(\text{PPh}_3)]$	2.834	78
$[\text{Cp}_2\text{Zr}\{\mu\text{-P}(\text{SiMe}_3)_2\}_2\text{Ni}(\text{CO})_2]$	3.038(1)	81
$[\text{Cp}_2\text{Zr}(\mu\text{-PEt}_2)\text{Ni}(\text{cod})]$		82
$[\text{Cp}_2\text{Zr}(\mu\text{-PEt}_2)_2\text{Ni}(\mu\text{-PEt}_2)_2\text{HfCp}_2]$	3.0186(8) ^a	82
$[\text{Cp}_2\text{Zr}(\mu\text{-PR}_2)_2\text{Pd}(\text{PR}'_3)]$ (R = Et, Cy; R' = Ph. R = Ph; R' = Ph, Me, Cy, OMe)		82
$[\text{Cp}_2\text{Zr}(\mu\text{-PR}_2)_2\text{Pt}(\text{PR}'_3)]$ (R = Et, Cy; R' = Ph. R = Ph; R' = Ph, OC ₆ H ₄ Me)		82
$[\text{Cp}_2\text{Zr}(\mu\text{-PPh}_2)\text{Pt}(\text{dmpe})]$		82
$[\text{Cp}_2\text{Hf}(\mu\text{-PEt}_2)_2\text{Ni}(\text{PR}_3)]$ (R = OC ₆ H ₄ Me, Cy)		82
$[\text{Cp}_2\text{Hf}(\mu\text{-PEt}_2)\text{NiL}_2]$ (L = PMe ₃ , P(OMe) ₃ , P(OC ₆ H ₄ Me-o) ₃)		82
$[\text{Cp}_2\text{Hf}(\mu\text{-PEt}_2)\text{NiL}_2]$ (L ₂ = cod, dmpe)		82
$[\text{Cp}_2\text{Hf}(\mu\text{-PPh}_2)\text{Pd}(\text{dmpe})]$	2.983(1)	82
$[\text{Cp}_2\text{Hf}(\mu\text{-PR}_2)_2\text{Pd}(\text{PR}'_3)]$ (R = Et, Cy; R' = Ph. R = Ph; R' = Ph, OC ₆ H ₄ Me)	2.896(1) (R, R' = Ph)	82
$[\text{Cp}_2\text{Hf}(\mu\text{-PR}_2)_2\text{Pt}(\text{PR}'_3)]$ (R = Et, Cy; R' = Ph. R = Ph; R' = Ph, Me, Cy, OMe)		82
$[(\text{OC})\text{Cp}_2\text{Nb}(\mu\text{-PR}_2)\text{Fe}(\text{CO})_3\text{L}]$ (R = Me, Ph; L = CO, PMe ₂ Ph)		83
$[\text{Cp}_2\text{Nb}(\mu\text{-PR}_2)(\mu\text{-CO})\text{Fe}(\text{CO})_3]$ (R = Me, Ph)	2.884(2) (R = Ph)	83
$[(\text{OC})\text{Cp}_2\text{Nb}(\mu\text{-PPhR})\text{Fe}(\text{CO})_4]$ (R = H, Me)		84
$[\text{Cp}_2\text{Nb}(\mu\text{-PPhR})(\mu\text{-CO})\text{Fe}(\text{CO})_3]$ (R = H, Me)		84
$[(\text{C}_5\text{H}_4\text{R})_2\text{Nb}(\mu\text{-PPh}_2)_2\text{Rh}(\text{C}_2\text{H}_4)]$ (R = H, Me)	2.869(2)	85
$[(\text{OC})_5\text{M}(\mu\text{-PPh}_2)\text{FeCp}(\text{CO})_2]$ (M = Cr, Mo, W)	4.1278(10) (M = Cr) 4.2250(6) (M = Mo)	88
$[\text{Cl}\{\text{Me}_2\text{C}(\text{C}_5\text{H}_4)_2\}_2\text{M}(\mu\text{-PPh}_2)\text{Fe}(\text{CO})_4]$ (M = Mo, W)	4.412(1) (M = W)	93
$[(\text{OC})_4\text{M}(\mu\text{-PPh}_2)_2\text{Ru}(\text{CO})_3]$ (M = Cr, Mo, W)		90
$[(\text{OC})_4\text{Mo}(\mu\text{-PPh}_2)_2\text{Fe}(\text{CO})_3]$	2.854(1)	94
$[(\text{OC})_2\text{CpMo}(\mu\text{-PPh}_2)\text{Fe}(\text{CO})_4]$	2.925(1)	87, 91
$[(\text{OC})_3\text{CpMo}(\mu\text{-PPh}_2)\text{Fe}(\text{CO})_4]$	4.246(6)	87
$[(\text{OC})_2\text{CpMo}(\mu\text{-PPh}_2)\text{Fe}(\text{CO})_3\text{L}]$ (L = P(OMe) ₃ , PPh ₂ , PPh ₃)	2.9295(5) (L = P(OMe) ₃)	87
$[(\text{OC})_4\text{W}(\mu\text{-PPh}_2)(\mu\text{-CO})\text{FeCp}(\text{CO})]$		88
$[(\text{OC})_4\text{LW}(\mu\text{-PPh}_2)\text{FeCp}(\text{CO})_2]$ (L = CO, MeCN, PMe ₃ , PPh ₂ , PPh ₃)	4.1812(11) (L = PMe ₃) 4.1757(15) (L = P(OMe) ₃)	86, 89
$[(\text{CO})_5\text{W}(\mu\text{-PPh}_2)\text{FeCp}(\text{CO})(\text{PMe}_3)]$	4.2741(10)	86
$[(\text{OC})_3\text{LW}(\mu\text{-PPh}_2)(\mu\text{-CO})\text{FeCp}(\text{CO})]$ (L = CO, PMe ₃ , P(OMe) ₃ , PPh ₂ , PPh ₃)	2.8548(11) (L = PPh ₃) 2.851(3) (L = CO)	86, 89
$[(\text{OC})_2\text{CpW}(\mu\text{-PPh}_2)(\mu\text{-CO})\text{Fe}(\text{CO})_3]$	2.8308(22)	92
$[(\text{OC})_2\text{CpW}(\mu\text{-PPh}_2)\text{Fe}(\text{CO})_3\text{L}]$ (L = P(OMe) ₃ , PMe ₃ , PPh ₂ , PPh ₃ , PEt ₃)	2.9588(10)	92
$[(\text{OC})_3\text{CpW}(\mu\text{-PPh}_2)\text{Fe}(\text{CO})_4]$	4.2434(20)	92
$[(\text{OC})_4\text{M}(\mu\text{-PPh}_2)_2\text{Rh}\{\text{C}(\text{=O})\text{CHMe}(\text{CH}_2)_n\text{PPh}_2\}]$ (M = Cr, Mo, W; n = 1, 2)	2.817(1) (M = W; n = 2)	272
$[(\text{OC})_2\text{CpM}(\mu\text{-PR}_2)\text{IrR}(\text{CO})_2(\text{PR}_3)]$ (M = Mo, W; R = Ph, Tol)	2.976(2) (M = Mo; R = Tol)	44, 95
$[(\text{OC})_2\text{CpMo}(\mu\text{-PPh}_2)\text{CoCp}(\text{CO})]$		91
$[(\text{OC})_4\text{M}(\mu\text{-PPh}_2)_2\{\mu\text{-OCCHMeCH}_2\text{PPh}_2\}\text{Rh}(\text{CO})]$ (M = Cr, Mo, W)	2.7311(9) (M = Cr)	272
$[(\text{OC})_4\text{M}(\mu\text{-PPh}_2)_2\{\mu\text{-OCCHMe}(\text{CH}_2)_2\text{PPh}_2\}\text{Rh}(\text{CO})]$ (M = Cr, Mo, W)	2.7788(9) (M = Mo)	272
$[(\text{OC})_2\text{CpMo}(\mu\text{-PTol}_2)\text{IrH}(\text{CO})_2(\text{PTol}_3)]$	2.957(1)	95
$[(\text{OC})_2\text{HCpMo}(\mu\text{-PTol}_2)\text{IrH}_2(\text{CO})_2(\text{PTol}_3)]$		95
$[(\text{OC})_4\text{W}(\mu\text{-PPh}_2)_2\text{RhH}(\text{CO})(\text{PPh}_3)]$		271
$[(\text{OC})_4\text{M}(\mu\text{-PPh}_2)_2\text{M}'(\text{PPh}_3)]$ (M = Cr, Mo; M' = Pd. M = Mo; M' = Pt)	2.748(1) (M = Mo; M' = Pd)	90
$[(\text{OC})_2\text{CpM}(\mu\text{-PR}_2)\text{Pd}(\text{PPh}_2)_2]$ (M = Cr, Mo, W; R = Cy, Ph)	2.916(2) (M = Mo; R = Cy)	100
$[(\text{OC})_5\text{M}(\mu\text{-PR}_2)\text{PtH}(\text{PPh}_3)_2]$ (M = Cr, Mo, W; R = Ph, ⁿ Pr)		101
$[(\text{OC})_4\text{M}(\mu\text{-H})(\mu\text{-PPh}_2)\text{PtL}_2]$ (M = Cr, Mo, W; L = PPh ₃ , PEt ₃ , PMe ₂ Ph)	2.905(2) (M = Cr; L = PEt ₃)	101
$[(\text{OC})_4\text{M}(\mu\text{-H})(\mu\text{-P}^n\text{Pr}_2)\text{Pt}(\text{PPh}_3)_2]$ (M = Cr, Mo, W)		101
$[(\text{OC})_5\text{M}(\mu\text{-PPh}_2)\text{PtH}(\text{cod})]$ (M = Cr, Mo, W)		101
$[(\text{OC})_4\text{M}(\mu\text{-PPh}_2)(\mu\text{-CO})\text{Pt}(\eta^3\text{-C}_8\text{H}_{13})]$ (M = Cr, Mo, W)	2.820(1) (M = Cr)	101
$[(\text{OC})_4\text{M}(\mu\text{-H})(\mu\text{-PPh}_2)\text{Pt}(\text{CO})(\text{PCy}_3)]$ (M = Cr, Mo, W)		101
$[(\text{Et}_3\text{P})(\text{OC})_3\text{M}(\mu\text{-PPh}_2)(\mu\text{-CO})\text{PtH}(\text{PCy}_3)]$ (M = Mo, W)		101
$[(\text{OC})_2\text{CpM}(\mu\text{-PPh}_2)\text{Pt}(\text{CO})(\text{PPh}_3)]$ (M = Mo, W)	2.810(1), 2.809(1) ^b (M = W)	103
$[(\text{OC})_2\text{CpM}(\mu\text{-PPh}_2)\text{PtL}_2]$ (M = Mo, W; L ₂ = (PPh ₃) ₂ , dppe)		103
$[(\text{OC})_2\text{CpM}(\mu\text{-PCy}_2)\text{PtL}(\text{PCy}_2\text{H})]$ (M = Mo, W; L = CO, PCy ₂ H, PCyH ₂)		98
$[(\text{OC})_2\text{CpM}(\mu\text{-H})(\mu\text{-PPh}_2)\text{Pt}(\text{PPh}_3)_2]^+$ (M = Mo, W)		103
$[(\text{OC})_2\text{CpM}(\mu\text{-H})(\mu\text{-PPh}_2)\text{PtCl}(\text{PPh}_3)]$ (M = Mo, W)		103
$[(\text{OC})_2\text{CpMo}(\mu\text{-H})(\mu\text{-PPh}_2)\text{Pt}(\text{CO})(\text{PPh}_3)]^+$		103
$[\{(\text{OC})_5\text{Mo}(\mu\text{-PPhPh})\}\text{Pt}(\text{diphos})]$ (diphos = dppe, dpae, Ph ₂ PCH=CHPPh ₂)		96

Table 6 (Continued)

	$r(\text{M}-\text{M})/\text{\AA}$	ref
$[(\text{OC})_4\text{Mo}(\mu\text{-PPh})_2\text{Pt}(\text{dppe})]$		96
$[(\text{OC})_5\text{Mo}(\mu\text{-PPh})\text{PtCl}(\text{PET}_3)_2]$	4.255	102
$[\{(\text{OC})_5\text{Mo}(\mu\text{-PPh})\}_2\text{Pt}(\text{PET}_3)_2]$	4.504(2), 4.573(2)	102
$[(\text{OC})_2\text{CpMo}(\mu\text{-H})(\mu\text{-PPh}_2)\text{PtCl}(\text{PPh}_3)]$		267
$[(\text{OC})_2\text{CpMo}(\mu\text{-H})(\mu\text{-PPh}_2)\text{Pt}(\text{MeCN})(\text{PPh}_3)]^+$		267
$[(\eta^7\text{-C}_7\text{H}_7)(\text{OC})\text{Mo}(\mu\text{-H})(\mu\text{-PCy}_2)\text{Pt}(\text{PPh}_3)_2]^+$		103
$[(\text{OC})_2\text{CpMo}(\mu\text{-PR}_2)(\mu\text{-H})\text{Pt}(\text{C}_4\text{H}_6\text{O})\text{L}]^+$ (R = Ph, Cy; L = PPh ₃ , PCy ₃)	3.063(1) (R = Ph; L = PCy ₃)	104
$[(\text{OC})_2(\text{C}_4\text{H}_6\text{O})\text{CpMo}(\mu\text{-PCyH})\text{PtH}(\text{PPh}_3)_2]^+$		104
$[(\text{OC})_2\text{CpMo}(\mu\text{-H})\{\mu\text{-PCy}(\text{C}_4\text{H}_7\text{O})\}\text{Pt}(\text{PPh}_3)_2]^+$		104
$[(\text{OC})_2\text{CpHW}(\mu\text{-PPh}_2)\text{Pt}(\text{CO})(\text{PPh}_3)]^+$		103
$[(\text{OC})_2\text{CpW}(\mu\text{-PPh}_2)\text{PtL}_2]$ (L = PPh ₃ , PPhPh ₂)		97
$[\{(\text{OC})_2\text{CpW}(\mu\text{-PPh}_2)\}_2\text{Pt}(\text{CO})]$		97
$[(\text{OC})_2\text{HCpW}(\mu\text{-PCy}_2)\text{Pt}(\text{CO})(\text{PCy}_2\text{H})]^+$		99
$[(\text{OC})_2\text{CpW}(\mu\text{-H})(\mu\text{-PCy}_2)\text{PtCl}(\text{PCy}_2\text{H})]$		99
$[(\text{ON})(\text{OC})\text{CpW}(\mu\text{-PCy}_2)\text{Pt}(\text{CO})(\text{PCy}_2\text{H})]^+$		99
$[(\text{ON})\text{CpW}(\mu\text{-PCy}_2)(\mu\text{-CO})\text{PtH}(\text{PCy}_2\text{H})]$		99
$[(\text{OC})_2\text{CpW}(\mu\text{-H})(\mu\text{-PCy}_2)\text{Pt}(\text{CO})(\text{PCy}_2\text{H})]^+$		99
$[(\text{OC})_2\text{CpW}(\mu\text{-PCy}_2)(\mu\text{-CuL})\text{Pt}(\text{CO})(\text{PCy}_2\text{H})]^+$ (L = MeCN, PPh ₃)		99
$[(\text{OC})_2\text{CpW}(\mu\text{-PCy}_2)\{\mu\text{-Ag}(\text{OTf})\}\text{Pt}(\text{CO})(\text{PCy}_2\text{H})]$		99
$[(\text{OC})_2\text{CpW}(\mu\text{-PCy}_2)\{\mu\text{-Au}(\text{PPh}_3)\}\text{Pt}(\text{CO})(\text{PCy}_2\text{H})]^+$	2.827(2) ^c	98

^a The zirconium and hafnium atoms are crystallographically disordered over the two early metal sites. ^b Two independent molecules per unit cell. ^c $r(\text{W}-\text{Pt})$.

have been obtained. The analogous vanadium(IV) complexes have also been prepared: the EPR spectra of $[\text{Cp}_2\text{V}(\mu\text{-SMe})_2\text{Cu}(\text{PR}_3)]^+$ show a hyperfine structure due to the coupling of the unpaired electron on vanadium to $^{63/65}\text{Cu}$ ($I = 3/2$, $a = 9.5$ G) and to ^{31}P ($a = 8.0$ G). The authors have cited this as evidence for electronic communication between the two metal centers.⁷⁴

Thiolato- and selenolato-bridged compounds have also been prepared by the reaction of RSSR (R = Me, Ph) or PhSeSePh with $[\text{Cp}^*\text{M}(\mu\text{-CO})_3\text{NiCp}^*]$ (M = Mo, W). The crystal structure of $[(\text{OC})(\text{PhS})\text{W}(\mu\text{-SPh})(\mu\text{-CO})\text{NiCp}^*]$ has been determined.⁷⁵

Treatment of the homoleptic uranium(IV) thiolate complex $[\text{U}(\text{SPh})_6]^{2-}$ with $[\text{Cu}(\text{SPh})_n]$ in the presence of excess triphenylphosphine afforded the bimetallic species $[\text{U}\{\mu\text{-SPh}_3\text{Cu}(\text{PPh}_3)_2\}]$. This was shown by X-ray crystal structure determination to have a U–Cu distance of 3.05 Å, which was considered by the authors as indicative of uranium–copper interaction (see section IV.A).⁷⁶

The titanium thiolate complex $[\text{Cp}_2\text{Ti}(\text{SPh})_2]$ will substitute the cyclooctadiene ligand in $[\text{Cp}^*\text{RuCl}(\text{cod})]$ to give $[\text{Cp}_2\text{Ti}(\mu\text{-SPh})_2\text{RuCp}^*\text{Cl}]$. The chloride ligand can be replaced by hydride or RCN (R = Me, ^tBu).⁷⁷

3. Phosphido-Bridged Compounds

Similarly, phosphido ligands have received much attention for their potential to bridge early–late heterobimetallic complexes (see Table 6).

The metalloalkyne complex $[\text{Cp}_2\text{Ti}(\mu\text{-C}\equiv\text{CPh})(\mu\text{-C}\equiv\text{CSiMe}_3)\text{Ni}(\text{PPh}_3)]$ was shown to react with triphenylphosphine in refluxing dioxane to give $[\text{Cp}_2\text{Ti}(\mu\text{-C}\equiv\text{CPh})(\mu\text{-PPh}_2)\text{Ni}(\text{PPh}_3)]$, which has a Ti–Ni distance of 2.834 Å. The authors note that this is only 0.13 Å longer than the sum of the metallic radii.⁷⁸

Choukroun, Royo, and co-workers have used the zirconium terminal phosphido complex $[(\text{C}_5\text{H}_4\text{SiMe}_3)_2\text{-Zr}(\text{PPh}_2)_2]$ as a diphosphine ligand in preparing

$[\{(\text{C}_5\text{H}_4\text{SiMe}_3)_2\text{Zr}(\mu\text{-PPh}_2)_2\text{Rh}\}_2(\mu\text{-S}^t\text{Bu})_2]$.⁷⁹ In a similar manner, Gelmini and Stephan have prepared $[\text{Cp}_2\text{M}(\mu\text{-PR}_2)\text{M}'\text{H}(\text{CO})(\text{PPh}_3)]$ (M = Zr, Hf; R = Ph, Cy; M' = Rh, Ir), and crystallographically characterized $[\text{Cp}_2\text{M}(\mu\text{-PPh}_2)\text{RhH}(\text{CO})(\text{PPh}_3)]$ (see also section VI.B).⁸⁰

The zirconocene phosphide $[\text{Cp}_2\text{Zr}\{\text{P}(\text{SiMe}_3)_2\}_2]$ displaces two carbonyl ligands from $[\text{Ni}(\text{CO})_4]$ to give $[\text{Cp}_2\text{Zr}\{\mu\text{-P}(\text{SiMe}_3)_2\}_2\text{Ni}(\text{CO})_2]$, which has been crystallographically characterized. Here also the Zr–Ni distance is slightly larger than the sum of the metallic radii. The ¹H NMR resonance of the cyclopentadienyl protons in the bimetallic complex is 0.6 ppm to higher field (increased shielding) than that of the starting material (see also section VI.F).⁸¹

Baker et al. have described the preparation, again starting from $[\text{Cp}_2\text{M}(\text{PPh}_2)_2]$, of over 40 group 4–group 10 phosphido-bridged heterobimetallic complexes, and obtained crystal structures for $[\text{Cp}_2\text{Zr}(\mu\text{-PET}_2)_2\text{-Ni}(\mu\text{-PET}_2)_2\text{HfCp}_2]$, $[\text{Cp}_2\text{Hf}(\mu\text{-PPh}_2)\text{Pd}(\text{PPh}_3)]$, and $[\text{Cp}_2\text{-Hf}(\mu\text{-PPh}_2)_2\text{Pd}(\text{dmpe})]$. All the metal–metal distances are close to 3 Å.⁸²

Group 5 terminal phosphido complexes have also been used in the preparation of heterobimetallic species. Thus, $[\text{Cp}_2\text{Nb}(\text{CO})(\text{PR}_2)]$ reacts with $\text{Fe}_2(\text{CO})_9$ to give a mixture of $[(\text{OC})\text{Cp}_2\text{Nb}(\mu\text{-PR}_2)\text{Fe}(\text{CO})_4]$ and $[\text{Cp}_2\text{Nb}(\mu\text{-CO})(\mu\text{-PR}_2)\text{Fe}(\text{CO})_3]$. Photolysis of the mono-bridged species gives the dibridged species, which has been crystallographically characterized. The Nb–Fe distance of 2.884 Å was considered by the authors to indicate the existence of a metal–metal bond. Extended Hückel molecular orbital calculations suggest that the bridging carbonyl plays a relatively large role in the interaction between the two metal centers. Use of a primary phosphido ligand gives very similar chemistry.⁸³

Treatment of the metallophosphonium salt $[\text{Cp}_2\text{-Nb}(\text{CO})(\text{PClHPh})]^+\text{Cl}^-$ with $[\text{Fe}(\text{CO})_4]^{2-}$ leads to substitution of chlorine and the formation of a mixture of $[(\text{OC})\text{Cp}_2\text{Nb}(\mu\text{-PPh})\text{Fe}(\text{CO})_4]$ and $[\text{Cp}_2\text{Nb}(\mu\text{-PPh})\text{-}$

(μ -CO)Fe(CO)₃]. The latter complex could be prepared quantitatively by UV irradiation of the former.⁸⁴

Reaction of the anionic niobium(III) complex [(C₅H₄R)₂Nb(PPh₂)₂]⁻ with [RhCl(cod)]₂ leads to fragmentation of the cyclooctadiene ligand and the formation of [(C₅H₄R)₂Nb(μ -PPh₂)₂Rh(C₂H₄)]. The X-ray crystal structure of the R = Me complex showed a Nb–Rh distance of 2.869 Å, which was taken to indicate the presence of a metal–metal bond.⁸⁵

The carbonyl bridge in [(OC)₄W(μ -PPh₂)(μ -CO)-FeCp(CO)] can readily be opened by a neutral ligand, giving [(OC)₄LW(μ -PPh₂)FeCp(CO)₂] (L = CO, MeCN, PMe₃, P(OMe)₃, PPh₂, PPh₃). Reaction of PMe₃ with the L = CO product leads to substitution of a carbonyl at the iron center. Thermolytic decarbonylation brings about the transfer of the phosphine ligand from iron to tungsten, giving [(OC)₄(Me₃P)W(μ -PPh₂)FeCp(CO)]. The same product is obtained by the photolytic decarbonylation of [(OC)₄(Me₃P)W(μ -PPh₂)FeCp(CO)₂].⁸⁶

The complex [(OC)₂CpMo(μ -PPh₂)Fe(CO)₄] is formed irreversibly by photolysis of [(OC)₃CpMo(μ -PPh₂)Fe(CO)₄]. One of the carbonyl ligands on iron can be substituted by a phosphine in the former complex.⁸⁷

The unstable group 6 phosphido complexes [M(CO)₅(PPh₂)]⁻ (M = Cr, Mo, W) can be prepared by deprotonation of [M(CO)₅(PPh₂H)]: their reaction with [CpFeI(CO)₂] gives [(OC)₅M(μ -PPh₂)FeCp(CO)₂].⁸⁸ The X-ray crystal structures of the chromium and molybdenum complexes unequivocally indicate the absence of a metal–metal bond, with M–Fe distances of more than 4 Å. Irradiation of the M = W complex leads to loss of carbon monoxide and the production of [(OC)₄W(μ -PPh₂)(μ -CO)Fe(CO)], which has a W–Fe distance of 2.851 Å. The ⁵⁷Fe Mössbauer spectra of the tungsten–iron complexes have also been reported.⁸⁹

A similar procedure has been used to prepare [(OC)₄M(μ -PPh₂)₂Ru(CO)₃] and [(OC)₄M(μ -PPh₂)₂M'(PPh₃)] (M = Cr, Mo, W; M' = Pd, Pt). The X-ray crystal structure of [(OC)₄Mo(μ -PPh₂)₂Pd(PPh₃)] has been obtained and shows an unusually short Mo–Pd distance of 2.748 Å, almost identical to the sum of the metallic radii (see also section VI.B).⁹⁰ Lindner et al. have also prepared [(OC)₂CpMo(μ -PPh₂)M(CO)₄] (M = Fe, Ru) and [(OC)₂CpMo(μ -PPh₂)CoCp(CO)] by a similar methodology.⁹¹

The reaction of [CpW(CO)₃(PPh₂)], prepared in situ, with [Fe₂(CO)₉] results in the phosphido-bridged compound [(OC)₃CpW(μ -PPh₂)Fe(CO)₄], which readily loses CO to afford [Cp(OC)₂W(μ -PPh₂)(μ -CO)Fe(CO)₃]. The X-ray crystal structures of these compounds show a short metal–metal distance in the latter (2.831 Å) but no tungsten–iron interaction in the former (4.243 Å). Addition of a phosphine ligand to the carbonyl-bridged species gives [(OC)₂CpW(μ -PPh₂)Fe(CO)₃L], in which the two metals are bridged only by the phosphido ligand and are separated, in the case of L = PPh₂H, by 2.959 Å. Hence, the loss of a neutral ligand from the tungsten center causes a reduction in the metal–metal distance of 1.3 Å, as the donation of electron density from the iron atom compensates for the loss of two electrons from the tungsten center.⁹²

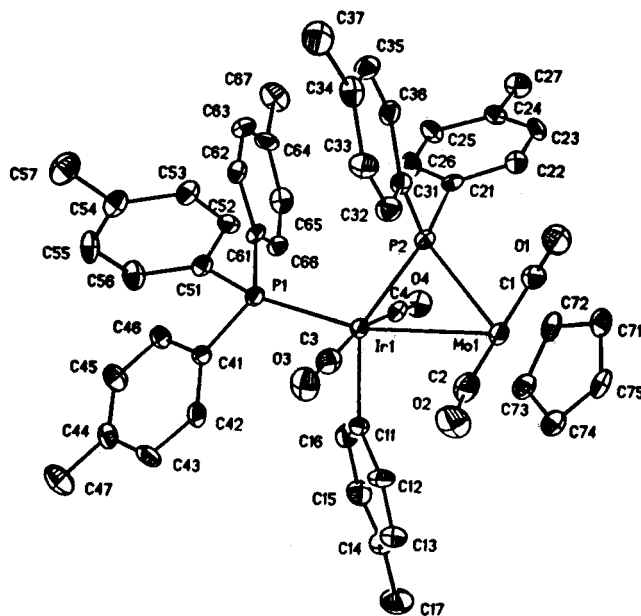


Figure 13. Crystal structure of [(OC)₂CpMo(μ -PPh₂)IrTol(CO)(PPh₃)]. Reprinted from ref 95. Copyright 1991 American Chemical Society.

Reaction of [Fe(PPh₂)(CO)₄]⁻ with the *ansa*-metallocene [{Me₂C(C₅H₄)₂}MCl₂] (M = Mo, W) affords the phosphido-bridged species [{Me₂C(C₅H₄)₂}CIM(μ -PPh₂)Fe(CO)₄], the X-ray crystal structure of the tungsten–iron compound of which has been determined. Use of a silicon-bridged *ansa*-metallocene leads to different chemistry (see section III.D.7).⁹³

The molybdenum–iron complex [(OC)₄Mo(μ -PPh₂)₂-Fe(CO)₃] can be prepared by direct reaction of [Fe(CO)₃(PPh₂)₂] and [Mo(CO)₆] (72 h, refluxing benzene). The mechanism of the reaction is unclear. The X-ray crystal structure of the product has been solved.⁹⁴

The condensation of [HMoCp(CO)₃] with [IrMe(CO)(PTol₃)₂] leads not only to elimination of methane but also to the cleavage of a phosphorus–carbon bond to give the 34-electron species [(OC)₂CpMo(μ -PTol₂)-IrTol(CO)₂(PTol₃)] (see Figure 13). The complex reacts with hydrogen, leading to the elimination of toluene and the formation of a mixture of [(OC)₂CpMo(μ -PTol₂)IrH(CO)₂(PTol₃)] and [(OC)₂HcPMo(μ -PTol₂)-Ir(H)₂(CO)₂(PTol₃)] in a 1:3 ratio.⁹⁵

The primary phosphido-bridged complex [{(OC)₅Mo(μ -PPhH)₂Pt(diphos)}] (diphos = dppe, dpae, Ph₂-PCH=CHPPh₂) was prepared by reaction of [Mo(CO)₅(PPhH)]⁻ with [PtCl₂(diphos)].⁹⁶ The two phosphorus atoms of the phosphido bridges are chiral, and the X-ray crystal structure of the *rac*-diastereomer has been solved. The *meso*-diastereomer is formed only in very small quantities, possibly due to unfavorable steric interactions between the phenyl ring of the phosphido bridge and the Mo(CO)₅ group. There is no direct molybdenum–platinum interaction in these complexes, and no distortion of the PtP₄ square plane occurs. Reaction of [Mo(CO)₄(PPhH)₂]²⁻ with [PtCl₂(diphos)] leads to the dibridged complex.⁹⁶

The tungsten terminal phosphido complex [CpW(PPh₂)(CO)₃] displaces the ethylene ligand of [Pt(C₂H₄)(PPh₃)₂] to produce the two phosphido-bridged complexes [(OC)₂CpW(μ -PPh₂)Pt(PPh₃)₂] and [(OC)₂CpW(μ -

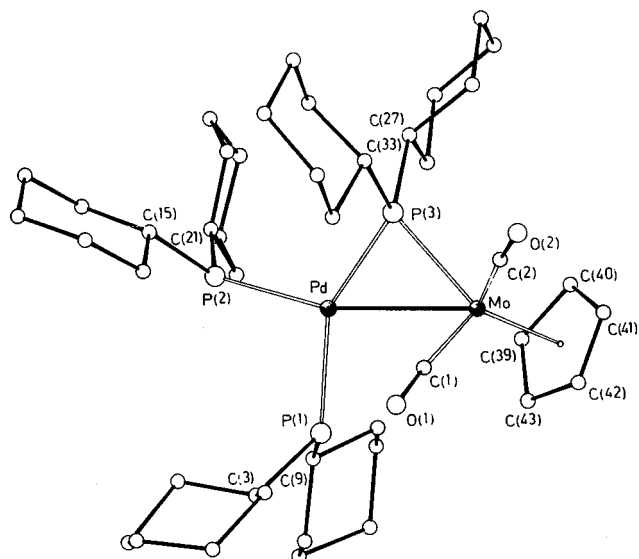


Figure 14. Crystal structure of $[(OC)_2CpMo(\mu-PCy_2)Pd(PCy_2H)_2]$. Reprinted from ref 100. Copyright 1989 Elsevier Science Ltd.

$PPh_2\}_2Pt(CO)]$.⁹⁷ The related complex $[(OC)_2CpW(\mu-PCy_2)Pt(CO)(PCy_2H)]$ reacts with the electrophilic group 11 fragments LCu^+ ($L = PPh_3, MeCN$), $(TfO)Ag$, or $(Ph_3P)Au^+$ to give complexes in which the group 11 atom bridges the tungsten–platinum framework. In this way, they behave in a manner completely isolobal to that of a bridging hydrogen.^{98,99}

The reaction of a secondary phosphine with $\{[(OC)_3CpM]_2Pd(PhCN)_2\}$ ($M = Cr, Mo, W$) prepared in situ yields the phosphido-bridged complexes $[(OC)_2CpM(\mu-PR_2)Pd(PHR)_2]$ ($R = Cy, Ph$; see Figure 14).¹⁰⁰

The oxidative addition of the P–H bond of $[M(CO)_5(PPh_2H)]$ ($M = Cr, Mo, W$) to $[Pt(C_2H_4)(PPh_3)_2]$ has been used to prepare $[(OC)_5M(\mu-PPh_2)PtH(PPh_3)_2]$. These complexes spontaneously lose CO on standing to give the phosphido–hydrido-bridged species $[(OC)_4M(\mu-PPh_2)(\mu-H)Pt(PPh_3)_2]$: this process is fully reversible. The PEt_3 and PMe_2Ph analogues have been prepared by substitution of chloride in $[PtHCl(PR_3)_2]$ by $[M(CO)_5(PPh_2)]^-$; these complexes also react with carbon monoxide to give the terminal hydrido species. The X-ray crystal structure of $[(OC)_4Cr(\mu-PPh_2)(\mu-H)Pt(PEt_3)_2]$ has been determined, and shows a Cr–Pt distance of 2.905 Å.¹⁰¹ The complexes $[M(CO)_5(PPh_2H)]$ ($M = Cr, Mo, W$) react with $[Pt(cod)_2]$ in the presence of ethylene to give the phosphido-bridged complexes $[(OC)_5M(\mu-PPh_2)PtH(cod)]$. These complexes rearrange rapidly with β -insertion of the hydride ligand into one of the cyclooctadiene double bonds to give $[(OC)_4M(\mu-PPh_2)(\mu-CO)Pt(\eta^3\text{-cyclooctenyl})]$, the chromium–platinum complex of which has been crystallographically characterized (see Figure 15).¹⁰¹ Addition of triphenylphosphine leads to β -elimination of hydride and substitution of the resulting cyclooctadiene ligand to give $[(OC)_4M(\mu-PPh_2)(\mu-H)Pt(CO)(PPh_3)]$. The mixed phosphine complexes $[M(CO)_4(PEt_3)(PPh_2H)]$ react with $[Pt(C_2H_4)(PCy_3)_2]$ to produce $[(OC)_3(Et_3P)M(\mu-PPh_2)(\mu-CO)PtH(PCy_3)]$: an isomer with a bridging hydride and a terminal carbonyl bound to platinum is also observed, in an equilibrium proportion of ca. 20% in

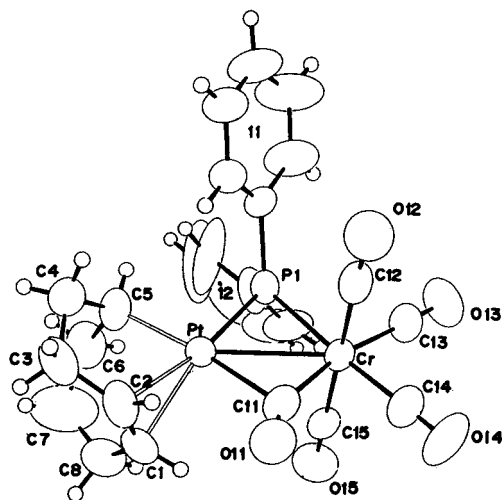


Figure 15. Crystal structure of $[(OC)_4Cr(\mu-PPh_2)(\mu-CO)Pt(\eta^3\text{-cyclooctenyl})]$. Reprinted from ref 101. Copyright 1989 American Chemical Society.

CD_2Cl_2 solution. A similar procedure has been used to prepare $[(OC)_5Mo(\mu-PPhH)PtCl(PEt_3)_2]$ and $\{[(OC)_5Mo(\mu-PPhH)]_2Pt(PEt_3)_2\}$ (the X-ray crystal structures of which have been determined)¹⁰² and has been extended to a number of other molybdenum and tungsten secondary phosphine complexes (see Table 6).^{103–105}

4. Substituted-Cyclopentadienyl-Bridged Compounds

Diphenylphosphino-substituted cyclopentadienyl ligands have been known for 20 years,¹⁰⁶ and have attracted considerable attention for the preparation of early–late heterobimetallic complexes (see Table 7). The ligands combine an organometallic portion, which is an excellent ligand for hard early metal centers, with a soft donor site which can coordinate to a late metal.

A good example of this chemistry is the zirconium–ruthenium complex $[ClZr(\mu-C_5Me_4PMe_2)_2(\mu-Cl)(\mu-H)RuH(PPh_3)]$, prepared by Baudry and co-workers and shown in Figure 16.¹⁰⁷ In effect, the zirconium portion of this molecule is acting as a diphosphine ligand for the ruthenium. The Zr–Ru distance of 3.13 Å appears to be determined by the geometry of the (dimethylphosphino)cyclopentadienyl ligands and not by any metal–metal interaction. The terminal hydrido and bridging chloro ligands interchange in solution. Substitution of a chloride ligand by a hydride on reaction with $NaBHET_3$ gives the trihydride $[ClZr(\mu-C_5Me_4PMe_2)_2(\mu-H)_2RuH(PPh_3)]$, which is also fluxional in solution.

The bis(thioether) metalloligand $[Ti(C_5H_4SMe)(C_7H_6SMe)]$ has been prepared in somewhat modest yield by the reaction of dimethyl disulfide with $[Ti(C_5H_4Li)(C_7H_6Li)]$. A platinum complex of this metalloligand has been tentatively claimed.¹⁰⁸

The zirconophosphines $[ZrCl_2(C_5H_4PPh_2)_2]$ and $[ZrCl_2\{(C_5H_4)_2PPh\}]$ react with $[PtPhX(cod)]$ ($X = Cl, Ph$) to give the *cis*- or *trans*- $[PtPhXP_2]$ type complexes. The complex $[Cl_2Zr(\mu-C_5H_4PPh_2)_2PtClPh]$ reacts slowly with carbon monoxide to give the corresponding benzoyl species (see section V.F).^{109,110}

The two titanophosphines $[TiX_2(C_5H_4PPh_2)_2]$ ($X = Cl, SPh$) react with the labile group 10 precursors

Table 7. Heterobimetallic Compounds with Monoanionic Substituted Cyclopentadienyl Bridges^a

	$r(\text{M}-\text{M}')/\text{\AA}$	ref
[XZr(μ -Cl)(μ -H)(μ -C ₅ Me ₄ PMe ₂) ₂ RuH(PPh ₃)] (X = Cl, H)	3.130(1) (X = Cl)	107, 120
[ClZr(μ -H) ₂ (μ -C ₅ Me ₄ PMe ₂) ₂ RuX(PPh ₃)] (X = Cl, H)		107
[X ₂ Ti(μ -C ₅ H ₄ PPh ₂) ₂ M(C ₆ F ₅) ₂] (X = Cl; M = Pd, Pt. X = SPh; M = Pt)		111
[Ti(μ -C ₅ H ₄ SMe)(μ -C ₇ H ₆ SMe)PtCl ₂]		108
[Cl ₂ Zr(μ -C ₅ H ₄ PPh ₂) ₂ PtX ₂] (X = Cl, Ph)		109, 110
[{Cl ₂ Zr[μ -(C ₅ H ₄) ₂ PPh]} ₂ PtX ₂] (X = Cl, Ph)		109, 110
[Cl ₂ Zr(μ -C ₅ H ₄ PPh ₂) ₂ PtCl(COPh)]		109, 110
[(OC) ₃ M(μ -C ₇ H ₇ CH ₂ COC ₅ H ₄)Fe(C ₅ H ₄ Ac)] (M = Cr, Mo)	nr (M = Mo)	140
[(OC) ₃ Cr(μ -C ₆ H ₅ C ₅ H ₄)RuCl(PPh ₃) ₂]	nr	117–119
[(OC) ₂ XCpW(μ -Ph ₂ PC ₅ H ₄)FeMe(CO) ₂] (X = Cl, Me)	nr (X = Me)	112
[(OC) ₃ CpW(μ -Ph ₂ PC ₅ H ₄)FeMe(CO) ₂] ⁺		112
[(OC) ₃ MeW(μ -C ₅ H ₄ PPh ₂)FeCpAc(CO)]	nr	112
[(OC) ₃ Cr(μ -C ₆ H ₅ C ₅ H ₄)Co(CO) ₂]	nr	117, 118
[(OC) ₃ M(μ -C ₅ H ₄ PPh ₂)PdI(PPh ₃)] (M = Mo, W)		113
[(OC) ₃ M(μ -C ₅ H ₂ Ph ₂ PPh ₂)PdX(PPh ₃)] (M = Mo, W; X = I, C≡CC ₆ H ₄ NO ₂)	2.831(1) (M = W; X = I)	114
[(OC) ₃ Mo(μ -C ₅ H ₄ PPh ₂)Ag] ₂	nr ^b	36
[(OC) ₃ M(μ -C ₅ H ₄ PPh ₂)M'] ₂ (M = Cr, Mo, W; M' = Ag, Au)	nr (M = Cr; M' = Ag) ^b	37
	nr (M = Mo; M' = Au) ^b	
	nr (M = W; M' = Ag) ^b	
[(thf) ₂ Yb(μ -C ₅ H ₄ PPh ₂)Ni(CO) ₂]	nr	116
[(thf) _n Yb(μ -C ₅ H ₄ PPh ₂) ₂ PtMe ₂] (n = 1, 2)	nr (n = 2)	115, 116

^a nr = not reported. ^b The unbridged metal–metal distances were reported (see Table 1).

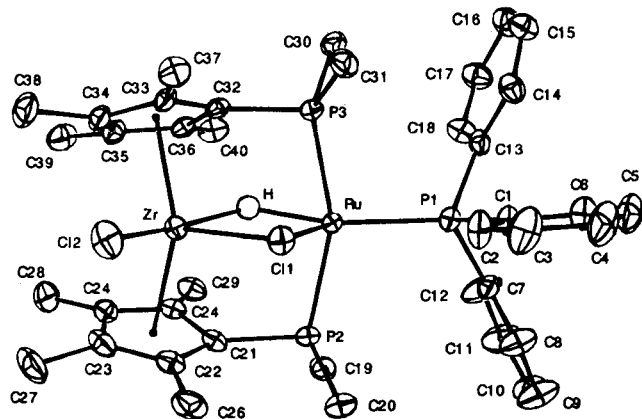


Figure 16. Crystal structure of [ClZr(μ -C₅Me₄PMe₂)₂(μ -H)(μ -Cl)RuH(PPh₃)]. Reprinted from ref 107. Copyright 1996 American Chemical Society.

[M(C₆F₅)₂(thf)₂] (M = Pd, Pt) with specific displacement of the THF by the phosphorus centers.¹¹¹

The group 8 metals, and iron in particular, are sufficiently hard to be strongly bound by cyclopentadienyl ligands, while group 6 metals form stable phosphine complexes. This has allowed Stille et al. to synthesize a range of tungsten–iron complexes in which the (diphenylphosphino)cyclopentadienyl bridge is in the “inverse” sense.¹¹² Hence, [FeMe(C₅H₄PPh₂)(CO)₂] reacts with [CpWX(CO)₂] fragments (X = Cl, Me, H) or with the cationic species [CpW(CO)₃]⁺ to afford [(OC)₂XCpW(μ -Ph₂PC₅H₄)FeMe(CO)₂] or [(OC)₃CpW(μ -Ph₂PC₅H₄)FeMe(CO)₂]⁺. The latter cationic complex can be methylated with methyl lithium to give the bimetallic tungsten acyl species [(OC)-CpAcW(μ -Ph₂PC₅H₄)FeMe(CO)₂]. Reaction of [WMe(C₅H₄PPh₂)(CO)₃] with [CpFeMe(CO)₂] leads to the “classically” bridged complex [(OC)₃MeW(μ -C₅H₄-PPh₂)FeAcCp(CO)].

Heterobimetallic complexes of molybdenum or tungsten with palladium can be obtained by oxidative addition of the M–I bond to a palladium(0) species. Hence, the complexes [(OC)₃M(μ -C₅H₂R₂PPh₂)PdI-

(PPh₃)] (R = H, Ph) have been prepared by reaction of [MI(C₅H₂R₂PPh₂)(CO)₃] with [Pd(PPh₃)₄].^{113,114} The X-ray crystal structure of the complex in which M = W and R = Ph shows a short tungsten–palladium distance of 2.83 Å. The iodide ligand can easily be substituted by reaction with a (trimethylstannyl)-alkyne (see section V.I).

The (diphenylphosphino)cyclopentadienyl complex [Yb(C₅H₄PPh₂)(thf)_n] has been prepared from [Yb(C₆F₅)₂] and C₅H₅PPh₂, and reacts with [Ni(CO)₂(PPh₃)₂] or [PtMe₂(cod)]: the X-ray crystal structures of the resulting heterobimetallic complexes, [(thf)₂Yb(μ -C₅H₄PPh₂)₂Ni(CO)₂] and [(thf)₂Yb(μ -C₅H₄PPh₂)₂-PtMe₂], have been determined.^{115,116}

A phenyl-substituted cyclopentadienyl ligand η^5 -coordinated to a late metal will bind a Cr(CO)₃ fragment in an η^6 -manner through the benzene ring. Hence, [(OC)₃Cr(μ -C₆H₅C₅H₄)RuCl(PPh₃)₂] and [(OC)₃-Cr(μ -C₆H₅C₅H₄)Co(CO)₂] have been prepared and crystallographically characterized (see Figure 17).^{117,118} The two metal centers adopt an anti-configuration, with the benzene ring and the cyclopentadienyl ring coplanar. The infrared and Raman spectra of these complexes have been extensively studied.¹¹⁹

Reaction of [(C₅Me₄PMe₂)₂ZrCl₂] with [RuH₂(H₂)-(PPh₃)₃] results in the formation of the bridged complex [Cl₂Zr(C₅Me₄PMe₂)₂RuH₂(PPh₃)], whose structure has been surmised from NMR data.¹²⁰

Addition of AgBF₄ or [AuCl(PPh₃)] to the anionic species [M(C₅H₄PPh₂)(CO)₃]⁻ (M = Cr, Mo, W) affords the cyclic compounds [(OC)₃M(μ -C₅H₄PPh₂)M']₂ (M' = Ag, Au), which also contain unbridged metal–metal bonds.³⁶

5. η^1 , η^x Bridges

Several complexes have been synthesized in which a cycloheptatrienyl ligand is σ -bonded through one carbon atom to a group 8 metal and η^6 -coordinated to a group 6 metal. The four complexes [{(OC)₃M(μ - η^6 , η^1 -C₇H₇)₂M'(CO)₄] (M = Cr, Mo; M' = Ru, Os) have been prepared, and the X-ray crystal structure

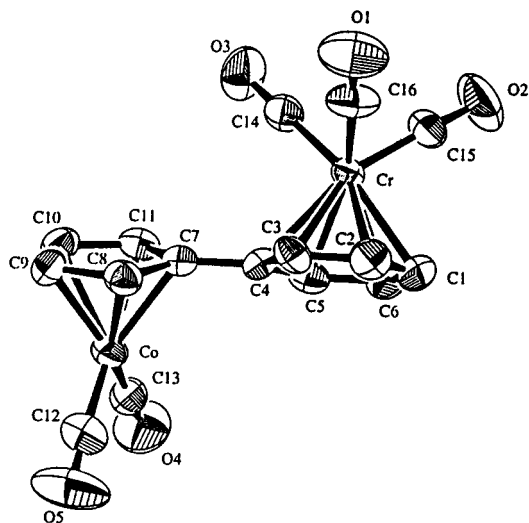


Figure 17. Crystal structure of $[(OC)_3Cr(\mu-C_6H_5C_5H_4)Co(CO)_2]$. Reprinted from ref 118. Copyright 1997 American Chemical Society.

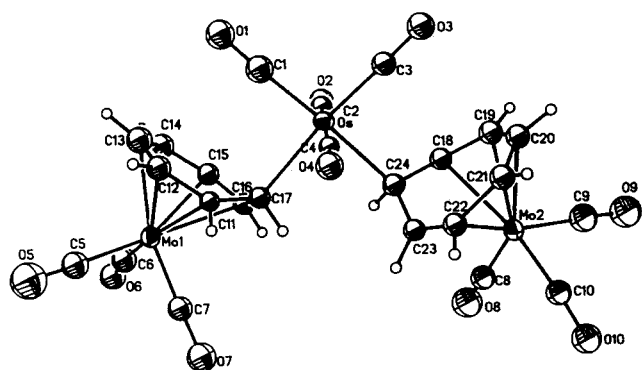


Figure 18. Crystal structure of $[(OC)_3Mo(\mu-C_7H_7)_2Os(CO)_4]$. Reprinted from ref 123. Copyright 1991 Wiley-VCH Verlag GmbH.

of the $M = Mo$, $M' = Os$ complex (Figure 18) shows that the η^6 part of the ligand is coplanar and that the two metals are very far from one another. In the same paper, a related set of complexes were described, bridged by η^1, η^2 -allyl ligands, for example, $[(OC)(ON)CpMo(\mu-\eta^2, \eta^1-C_3H_5)_2Os(CO)_4]$.¹²¹

The group 8 metal carbonyl anions $[CpM(CO)_2]^-$ ($M = Fe, Ru$) will attack the tropylium ring of $[(\eta^7-C_7H_7)M'(CO)_3]^+$ ($M' = Cr, Mo, W$) to give the cycloheptatrienyl-bridged compounds $[(OC)_3M'(\mu-\eta^6, \eta^1-C_7H_7)MCp(CO)_2]$. Thermal loss of carbon monoxide from the ruthenium complexes leads to the metal–metal bonded species $[(C_7H_7)(OC)_2M'RuCp(CO)_2]$ in low yield.¹²² Nucleophilic attack in the opposite sense with the tungsten nucleophile $[CpW(CO)_3]^-$ has allowed Niemer et al. to prepare the complex $[(OC)_3CpW(\mu-\eta^1_W, \eta^4_{Fe-cyclohexadienyl})Fe(CO)_3]$.¹²³

In η^1, η^7 -cycloheptatrienyl complexes, the η^1 -carbon atom is almost always sp^3 -hybridized and does not take part in the η^6 -coordination of the other metal. However, one example is known in which the η^1 -coordination (to iron) is from an sp^2 carbon atom. The synthesis of this compound is unusual in that the cycloheptatriene ring is first σ -bonded to iron; only then is the chromium center attached to the three double bonds in an η^6 manner. The X-ray crystal structure (Figure 19) shows that the CH_2 group of

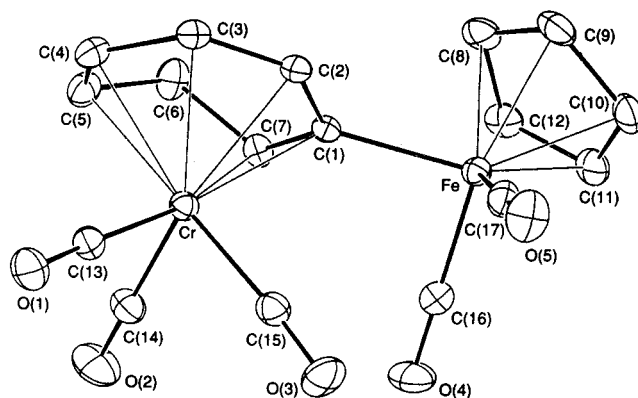


Figure 19. Crystal structure of $[(OC)_3Cr(\mu-C_7H_7)FeCp(CO)_2]$. Reprinted from ref 124. Copyright 1997 Royal Society of Chemistry.

the cycloheptatriene ring is accessible for hydride abstraction, and reaction of the compound with the triphenylcarbonium ion, Ph_3C^+ , leads to the cycloheptatrienylidene-bridged complex.¹²⁴

A similar type of bridging system is the η^1, η^6 -phenyl ligand. A series of chromium–iron complexes has been prepared by the nucleophilic substitution of fluorine in $[Cr(\eta^6-C_6H_5F)(CO)_5]$ by $[CpFe(CO)_2]^-$. The complexes with Cp' or η^5 -indenyl in place of Cp , or with η^1, η^6 -*p*-tolyl bridges, have also been synthesized by this strategy and crystallographically characterized.¹²⁵ An analogous approach has been used in the case of cobalt, where an unidentified nucleophilic species is prepared by reaction of $NaBH_4$ with $[CoCl(dmg)_2(py)]$. This is then reacted with $[Cr(CO)_3(\eta^6-C_6H_5CH_2Cl)]$ or $[Cr(CO)_3(\eta^6-ClCH_2C_6H_4CH_2Cl-p)]$. The X-ray crystal structure of the η^1, η^6 -benzyl bridged complex $[(OC)_3Cr(\mu-C_6H_5CH_2)Co(dmg)_2(py)]$ has been determined.¹²⁶

It is also possible to start with σ -phenyl or σ -benzyl complexes of a late transition metal and to attach the early metal fragment by reaction with, e.g., $[Cr(CO)_3(MeCN)_3]$. Hence, the iridium complexes $[IrPh(dmb)_2]$ and $[IrBz(dmb)_2]$ ($dmb = 2,3$ -dimethylbutadiene) have been coordinated in an η^6 -manner to $M(CO)_3$ fragments ($M = Cr, Mo$).¹²⁷ Finally, $[Cr(CO)_3(\eta^6-C_6H_6)]$ can be directly lithiated by butyllithium in THF, and the resulting species reacted with $[AuCl(PPh_3)]$ to produce a chromium–gold heterobimetallic complex.¹²⁸

6. LX-Type Bridges

A cyclic tetranuclear species, $[Cp_2Ti(\mu-OCOC_5H_4N-\kappa_{Ti}O, \kappa_{Pt}M)PtL_2]_2^{4+}$, ($L_2 = (PEt_3)_2, dppp$) is formed by self-assembly on reaction of $[Cp_2Ti(\eta^1-OCOC_5H_4N-O)_2]$ with $[Pt(OTf)_2L_2]$.¹²⁹ The opposite approach has been used to prepare hydroxypyridine-bridged species. *N*-Bound hydroxypyridine complexes of platinum can be easily deprotonated, and the resulting anions reacted with Cp_2TiCl_2 . The X-ray crystal structure of $[Cp_2TiTi(\mu-OC_5H_4N-\kappa_{Ti}O, \kappa_{Pt}M)PtCl_2(dmsO)]$ has been determined (see Figure 20).¹³⁰

Alcoholysis of $[Cp^*ZrMe_3]$ by $[PtMe_2(Ph_2PCH_2OH-P)_2]$ gives the heterobimetallic complex $[Cp^*MeZr(\mu-OCH_2PPh_2-\kappa_{Zr}O, \kappa_{Pt}P)_2PtMe_2]$. Isotopic substitution with deuterium showed that methyl transfer between the two metal centers is facile. Indeed, when $[Cp^*Zr-$

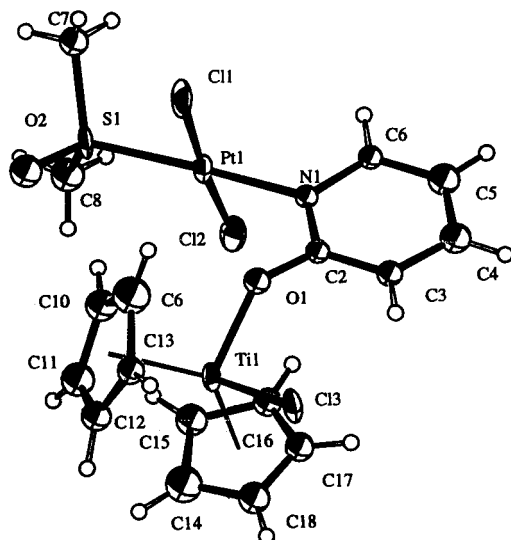


Figure 20. Crystal structure of $[\text{ClCp}_2\text{Ti}(\mu\text{-OC}_5\text{H}_4\text{N})\text{PtCl}_2(\text{dmsO})]$. Reprinted from ref 130. Copyright 1993 American Chemical Society.

Me_3] is reacted with $[\text{Cp}^*\text{RhCl}_2(\text{Ph}_2\text{PCH}_2\text{OH}-P)]$, complete methyl transfer from zirconium to rhodium occurs, leading to $[\text{Cp}^*\text{Cl}_2\text{Zr}(\mu\text{-OCH}_2\text{PPh}_2\text{-}i\kappa\text{Zr}, O, \kappa\text{Rh}-P)\text{-RhMe}_2\text{Cp}^*]$. The permethylated zirconium–rhodium complex can be obtained by reaction with MeMgBr .¹³¹

The hydroxyphosphine bridge can also be formed by reaction of $[\text{Cp}^*\text{ZrMe}_3]$ with the free ligand before attachment of the second metal center. When $[\text{Cp}^*\text{ZrMe}(\text{OCH}_2\text{PPh}_2\text{-}O)_2]$ formed in this manner is reacted with $[\text{RhCl}(\text{CO})_2]_2$, methyl transfer and migratory insertion of carbon monoxide occur, giving $[\text{Cp}^*\text{Zr}(\mu\text{-OCH}_2\text{PPh}_2\text{-}i\kappa\text{Zr}, O, \kappa\text{Rh}-P)_2(\mu\text{-OCMe-}i\kappa\text{Zr}, O, \kappa\text{Rh}-C)(\mu\text{-Cl})\text{-Rh}(\text{CO})]$. A similar methyl transfer occurs on reaction of $[\text{Cp}^*\text{ZrMe}(\text{OCH}_2\text{PPh}_2\text{-}O)_2]$ with $[\text{RhH}(\text{PPh}_3)_3]$, but in this case it is followed by reductive elimination of methane to produce $[\text{Cp}^*\text{Zr}(\mu\text{-OCH}_2\text{PPh}_2\text{-}i\kappa\text{Zr}, O, \kappa\text{Rh}-P)_2\text{-Rh}(\text{PPh}_3)]$. This is formally a zirconium(III)–rhodium(0) species which appears to contain a metal–metal bond. The X-ray crystal structure of the related compound $[\text{Cp}^*\text{Zr}(\mu\text{-OCH}_2\text{PPh}_2\text{-}i\kappa\text{Zr}, O, \kappa\text{Rh}-P)_2\text{RhMe}_2]$, formally zirconium(III)–rhodium(II), gives strong evidence (supported by EHMO calculations) for a metal–metal bond, with a Zr–Rh distance of only 2.444 Å. Indeed, the authors have postulated the existence of a metal–metal multiple bond in this system (see section IV).¹⁴

The compounds $[(\text{OC})_5\text{M}(\mu\text{-NC}_5\text{H}_4\text{CH}=\text{CH}-\text{C}\equiv\text{C-}\kappa\text{M}, \kappa\text{Ru})\text{Ru}(\eta^5\text{-indenyl})(\text{PPh}_3)]$ and $[(\text{OC})_5\text{M}(\mu\text{-NCC}_6\text{H}_4\text{CH}=\text{CH}-\text{C}\equiv\text{C-}\kappa\text{M}, \kappa\text{Ru})\text{Ru}(\eta^5\text{-indenyl})(\text{PPh}_3)]$ ($\text{M} = \text{Cr}, \text{W}$) have been prepared and their nonlinear optical properties examined. Although the latter compounds showed a relatively high hyperpolarizability, this is not as high as that for certain monometallic ruthenium compounds.¹³²

Reaction of $[\text{Cr}(\text{CO})_6]$ with $[\text{Fe}(\eta^5\text{-C}_5\text{R}_5)(\text{SiMe}_2\text{SiMe}_2\text{-Ph-}i\text{Si})(\text{CO})_2]$ ($\text{R} = \text{H}, \text{Me}$) leads to the silylphenyl-bridged compound $[(\text{OC})_3\text{Cr}(\mu\text{-}\eta^6\text{Cr}, \eta^1\text{Fe-C}_6\text{H}_5\text{SiMe}_2\text{-SiMe}_2\text{-}\kappa\text{Fe}, i\text{Si})\text{Fe}(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2]$. On irradiation, this compound transforms into $[(\text{OC})_2\text{Cr}(\mu\text{-SiMe}_2)(\mu\text{-}\eta^6\text{Cr}, \eta^1\text{Fe-C}_6\text{H}_5\text{SiMe}_2\text{-}\kappa\text{Fe}, i\text{Si})\text{Fe}(\eta^5\text{-C}_5\text{R}_5)(\text{CO})]$ (see Figure 21). This transformation appears to proceed via a terminal silylene intermediate, and on further

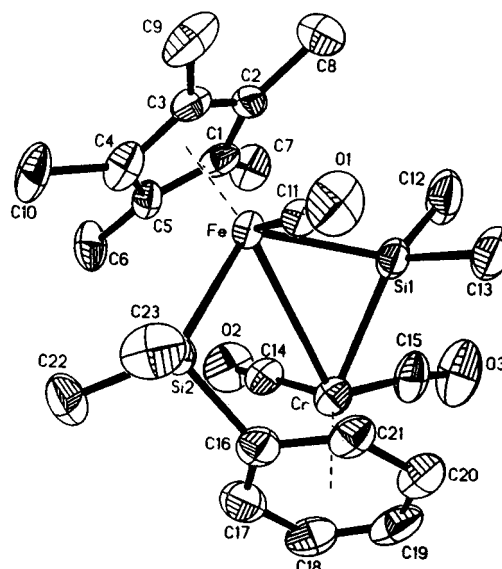


Figure 21. Crystal structure of $[(\text{OC})_2\text{Cr}(\mu\text{-SiMe}_2)(\mu\text{-C}_6\text{H}_5\text{-SiMe}_2)\text{FeCp}^*(\text{CO})]$. Reprinted from ref 133. Copyright 1997 American Chemical Society.

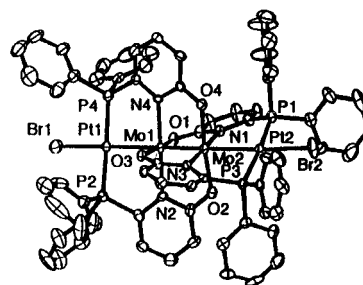


Figure 22. Crystal structure of $[\text{BrPd}(\mu\text{-pyphos})_2\text{MoMo}(\mu\text{-pyphos})_2\text{PdBr}]$. Reprinted from ref 136. Copyright 1996 American Chemical Society.

irradiation in the presence of CO $[(\text{OC})_3\text{Cr}(\mu\text{-}\eta^6\text{Cr}, \eta^1\text{Fe-C}_6\text{H}_5\text{SiMe}_2\text{-}\kappa\text{Fe}, i\text{Si})\text{Fe}(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2]$ is formed (see section V.M).¹³³

The ligand 6-(diphenylphosphino)-2-pyridonate (pyphos^-) imposes a relatively short distance between the two metal centers that it bridges. Its dinuclear complexes of group 6 metals, $[\text{M}_2(\text{pyphos})_4]$ ($\text{M} = \text{Cr}, \text{Mo}$), retain four phosphorus centers which are free to coordinate palladium(II) or platinum(II) fragments, giving $[\text{X}_2\text{M}'(\mu\text{-pyphos})_2\text{MM}(\mu\text{-pyphos})_2\text{M}'\text{X}_2]$ ($\text{M} = \text{Cr}, \text{Mo}$; $\text{M}' = \text{Pd}, \text{Pt}$; $\text{X} = \text{Cl}, \text{Br}, \text{Me}$).¹³⁴ Mashima et al. do not consider that these $\text{M}(\text{II})\text{-M}'(\text{II})$ complexes contain $\text{M-M}'$ bonding, although it is noteworthy that the Cr–Cr distance in $[\text{Me}_2\text{Pt}(\mu\text{-pyphos})_2\text{CrCr}(\mu\text{-pyphos})_2\text{PtMe}_2]$, 2.389 Å, is significantly longer than that in $[\text{Cr}_2(\text{pyphos})_4]$ (2.015 Å).¹³⁵ Reduction of the late metal centers leads to the formation of $[\text{XM}'(\mu\text{-pyphos})_2\text{MM}(\mu\text{-pyphos})_2\text{M}'\text{X}]$, in which the separation between the early and the late metal centers is reduced (e.g., 2.687 Å rather than 2.902 Å for $\text{M} = \text{Mo}$, $\text{M}' = \text{Pd}$, and $\text{X} = \text{Br}$; see Figure 22). These systems have attracted interest for the preparation of low-dimensional materials.¹³⁶

The phosphoranimes $\text{Ph}_2\text{PCH}_2\text{PPh}_2=\text{NSiMe}_3$ and $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{PPh}_2=\text{NSiMe}_3$ react with $[\text{CpTiCl}_3]$ and $[\text{PdCl}_2(\text{PhCN})_2]$ in either order with elimination of Me_3SiCl to give the phosphoranimo-bridged complexes $[\text{CpCl}_2\text{Ti}\{\mu\text{-N}=\text{PPh}_2(\text{CH}_2)_n\text{EPH}_2\text{-}\kappa\text{Ti}, \kappa\text{Pd}, \text{N}$,

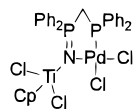


Figure 23. Proposed structure of the phosphoranimido-bridged complex $[\text{Cl}_2\text{CpTi}(\mu\text{-N}=\text{PPh}_2\text{CH}_2\text{PPh}_2)\text{PdCl}_2]$. Redrawn from ref 137.

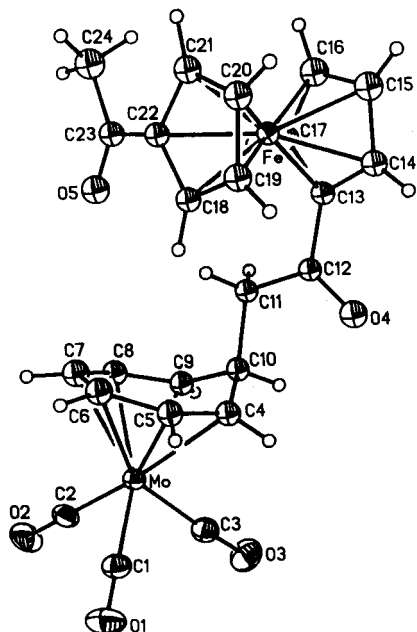


Figure 24. Crystal structure of $[(\text{OC})_3\text{Mo}(\mu\text{-C}_7\text{H}_7\text{CH}_2\text{COC}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_4\text{COMe})]$. Reprinted from ref 140. Copyright 1991 Elsevier Science Ltd.

$\kappa_{\text{Pd}}E_j\text{PdCl}_2]$ ($E = \text{P}$, $n = 1$; $E = \text{As}$, $n = 2$) (Figure 23).¹³⁷

The zirconium bis(metallophosphine) $[(^t\text{BuC}_5\text{H}_4)_2\text{Zr}(\text{CH}_2\text{PPh}_2)_2]$ reacts with the labile rhodium precursors $[\text{Rh}(\text{cod})(\text{PPh}_3)_2]^+$ and $[\text{Rh}_2(\mu\text{-S}^t\text{Bu})_2(\text{CO})_4]$ in a manner similar to that of organodiphosphine ligands, giving $[(^t\text{BuC}_5\text{H}_4)_2\text{Zr}(\mu\text{-CH}_2\text{PPh}_2\text{-}\kappa_{\text{Zr}}\text{C}, \kappa_{\text{Rh}}\text{P})_2\text{Rh}(\text{cod})]^+$ and $[(^t\text{BuC}_5\text{H}_4)_2\text{Zr}(\mu\text{-CH}_2\text{PPh}_2\text{-}\kappa_{\text{Zr}}\text{C}, \kappa_{\text{Rh}}\text{P})_2\text{Rh}_2(\text{S}^t\text{Bu})_2(\text{CO})_2]$. The latter complex has been crystallographically characterized.¹³⁸ The complexes $[\text{Cp}_2\text{Zr}(\mu\text{-CH}_2\text{PPh}_2)_2\text{Rh}(\text{acac})(\text{CO})_n]$ ($n = 1, 2$) and $[\{\text{Cp}_2\text{Zr}(\mu\text{-CH}_2\text{PPh}_2)_2\}_{12-x}\text{Rh}_x(\text{CO})_x]$ ($x = 8\text{--}11$) have been claimed on the basis of spectroscopic observation of mixtures of $[\text{Cp}_2\text{Zr}(\text{CH}_2\text{PPh}_2)_2]$ and $[\text{Rh}(\text{acac})(\text{CO})_2]$ under hydroformylation conditions.¹³⁹

Nucleophilic attack of the organometallic enolate anions $[(\eta^5\text{-C}_5\text{H}_4\text{Ac})\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{COCH}_2)]^-$ and $[\text{CpFe}(\text{COCH}_2)(\text{CO})(\text{PPh}_3)]^-$ on the tropylium ring of $[(\eta^7\text{-C}_7\text{H}_7)\text{M}(\text{CO})_3]^+$ ($\text{M} = \text{Cr}, \text{Mo}$) gives the heterobimetallic complexes $[(\text{CO})_3\text{M}(\mu\text{-C}_7\text{H}_7\text{CH}_2\text{COC}_5\text{H}_4\text{-}\kappa_{\text{M}}\text{C}_7\text{H}_7(\eta^7), \kappa_{\text{Fe}}\text{C}_5\text{H}_4(\eta^5))\text{Fe}(\text{C}_5\text{H}_4\text{Ac})]$ and $[(\text{CO})_3\text{M}(\mu\text{-C}_7\text{H}_7\text{CH}_2\text{CO-}\kappa_{\text{M}}\text{C}_7\text{H}_7(\eta^7), \kappa_{\text{Fe}}\text{C})\text{FeCp}(\text{CO})(\text{PPh}_3)]$. The X-ray crystal structure of the former molybdenum-iron complex has been determined (see Figure 24).¹⁴⁰

The labile molybdenum precursor $[\text{Mo}(\text{CO})_4(\text{nbd})]$ reacts with the nickel phosphinothiolate complex $[\text{Ni}(\text{SCH}_2\text{CH}_2\text{PPh}_2)_2]$ to form the sulfur-bridged bimetallic species $[(\text{CO})_4\text{Mo}(\mu\text{-SCH}_2\text{CH}_2\text{PPh}_2\text{-}\kappa_{\text{Mo}}\text{S}, \kappa_{\text{Ni}}\text{S}, \kappa_{\text{Ni}}\text{P})_2\text{Ni}]$, the X-ray crystal structure of which has been obtained.¹⁴¹ The longer chain phosphinothiolate $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{SH}$ has also been used as a bridging ligand in heterobimetallic complexes: its titanocene derivative

$[\text{Cp}_2\text{Ti}\{\text{S}(\text{CH}_2)_3\text{PPh}_2\text{-S}\}_2]$ acts as a metalloligand for nickel(0), and the resulting compound, $[\text{Cp}_2\text{Ti}\{\mu\text{-S}(\text{CH}_2)_3\text{PPh}_2\text{-}\kappa_{\text{Ti}}\text{S}, \kappa_{\text{Ni}}\text{S}, \kappa_{\text{Ni}}\text{P}\}\text{Ni}]$, has been crystallographically characterized.¹⁴² Carbonylation of this complex gives $[\text{Cp}_2\text{Ti}\{\mu\text{-S}(\text{CH}_2)_3\text{PPh}_2\}\text{Ni}(\text{CO})_2]$, in which the metal centers are nearly 7 Å from one another. The titanium(IV)-palladium(II) complex $[\text{Cp}_2\text{Ti}\{\mu\text{-S}(\text{CH}_2)_3\text{PPh}_2\text{-}\kappa_{\text{Ti}}\text{S}, \kappa_{\text{Pd}}\text{S}, \kappa_{\text{Pd}}\text{P}\}\text{Pd}]^{2+}$ has also been prepared.¹⁴²

7. Metalloalkyne Complexes

A large group of carbon-bridged heterobimetallic compounds are the so-called pincer complexes, in which two acetylenic fragments are σ -bonded to an early metal center and η^2 -bound to a late metal center. Lang and co-workers have mostly worked with $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\eta^1\text{-C}\equiv\text{CR})_2]$ ($\text{R} = \text{SiMe}_3, \text{Ph}$), and have associated this metalloligand with FeCl_2 , CuCl , $\text{Co}(\text{CO})$, $\text{Ni}(\text{CO})$, and $\text{Pd}(\text{PPh}_3)$ fragments.^{143,144} The angle between the two acetylenic fragments is 102.8° in the free ligand: this is reduced on coordination to between 85° and 95° . There does not seem to be a relation between this angle and the distance between the two metal centers. In the case of $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\mu\text{-C}\equiv\text{CPh})_2\text{Co}(\text{CO})]$ (see Figure 25),

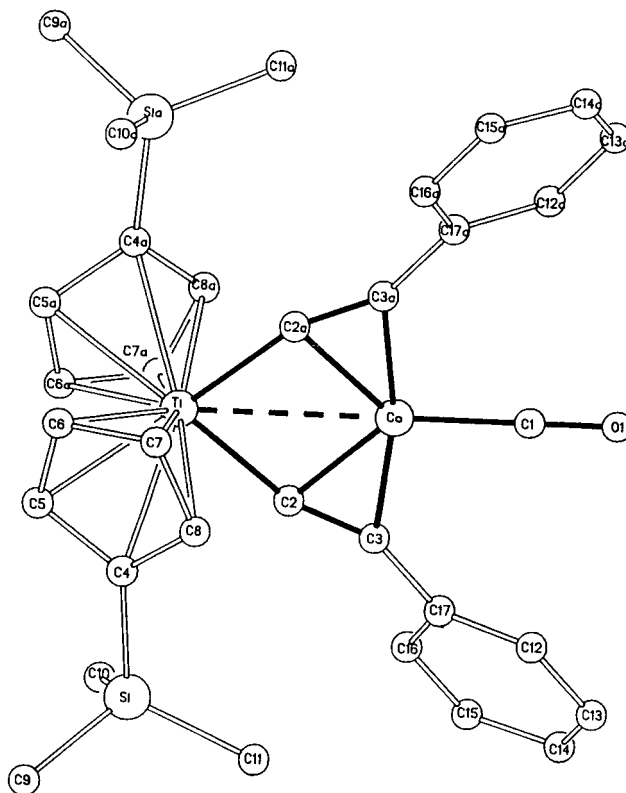


Figure 25. Crystal structure of $[(\text{C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\mu\text{-C}\equiv\text{CPh})_2\text{Co}(\text{CO})]$. Reprinted from ref 144. Copyright 1991 Elsevier Science Ltd.

this distance is as short as 2.819 Å.¹⁴⁴ A similar complex containing only one acetylenic fragment has been prepared: $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\mu\text{-C}\equiv\text{CSiMe}_3)(\mu\text{-Cl})\text{CuX}]$ ($\text{X} = \text{Cl}, \text{Br}$).¹⁴⁵ Polyacetylenic fragments have also been used: the two metalloligands $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\text{C}\equiv\text{C}-\text{C}\equiv\text{CET})]$ and $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\text{C}\equiv\text{CSiMe}_2\text{C}\equiv\text{CSiMe}_3)_2]$ react as previously to bind $\text{M}(\text{PPh}_3)$ fragments ($\text{M} = \text{Pd}, \text{Pt}$). However, the latter

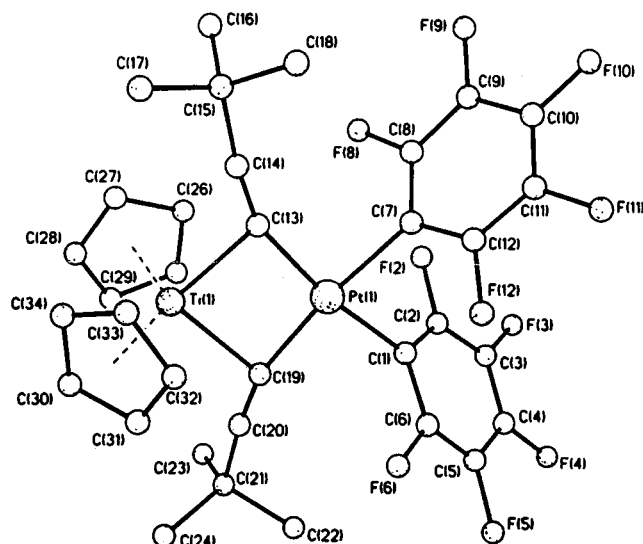


Figure 26. Crystal structure of $[\text{Cp}_2\text{Ti}(\mu\text{-C}\equiv\text{C}^t\text{Bu})_2\text{Pt}(\text{C}_6\text{F}_5)_2]$. Reprinted from ref 148. Copyright 1993 American Chemical Society.

ligand reacts with 4 equiv of $\text{Co}_2(\text{CO})_8$ to bind a $\text{Co}_2(\text{CO})_6$ fragment to each of the four carbon-carbon triple bonds.¹⁴⁶

A cross-coupling reaction can be observed between $[\text{Cp}_2\text{Zr}(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)]$ and $[\text{Ni}(\text{PPh}_3)_2(\eta^2\text{-Me}_3\text{SiC}\equiv\text{C}-\text{C}\equiv\text{CSiMe}_3)]$ with the elimination of bis(trimethylsilyl)acetylene and triphenylphosphine to give $[\text{Cp}_2\text{Zr}(\mu\text{-}\eta^1\text{Zr}, \eta^2\text{Ni-C}\equiv\text{CSiMe}_3)(\mu\text{-}\eta^2\text{Zr}, \eta^1\text{Ni-Me}_3\text{SiC}\equiv\text{C})\text{Ni}(\text{PPh}_3)]$.¹⁴⁷

Another bridging mode for acetylenic fragments is shown by the compound $[\text{Cp}_2\text{Ti}(\mu\text{-C}\equiv\text{C}^t\text{Bu})_2\text{Pt}(\text{C}_6\text{F}_5)_2]$. The acetylide bridges are end-bound, leading to a three-center two-electron bond (see Figure 26).¹⁴⁸ The X-ray crystal structure shows a slight asymmetry in the bridge, with the carbon atom being closer to the platinum than to the titanium ($r(\text{Pt}-\text{C}) \approx 2.01 \text{ \AA}$, $r(\text{Ti}-\text{C}) \approx 2.25 \text{ \AA}$). A similar bridging arrangement has been claimed for the compound $[(\text{OC})_3\text{W}(\mu\text{-C}\equiv\text{CH})(\mu\text{-dppm})_2\text{Pt}(\text{C}\equiv\text{CH})]$.¹⁴⁹

8. Indenyl-Bridged Compounds

A wide variety of $[(\text{OC})_3\text{Cr}(\mu\text{-indenyl})\text{RhL}_2]$ complexes have been prepared by Ceccon et al. (see Table 8). The chromium and the rhodium centers can sit either on the same face or on opposite faces of the indenyl ring. The complexes are synthesized by the

reaction of a rhodium(I) precursor, e.g., $[\text{RhCl}(\text{cod})]_2$, with a deprotonated ($\eta^6\text{-indenyl}$)chromium complex.^{150,151} Spectroscopic studies indicate that the coordination of the $\text{Cr}(\text{CO})_3$ fragment to the six-membered ring of the indenyl ligand causes the coordination of the rhodium to be closer to η^3 than in monometallic (indenyl)rhodium complexes.¹⁵²⁻¹⁵⁷

Very recently, the analogous chromium-iridium compounds have been described. Structurally, $[(\text{OC})_3\text{Cr}(\mu\text{-indenyl})\text{Ir}(\text{cod})]$ is similar to its rhodium analogue, but its reactivity toward carbon monoxide is somewhat different (see section V.F).¹⁵⁸

9. Halide- and Other Monoanionic-Bridged Compounds

Although halide-bridged homobimetallic compounds are a common feature of the chemistry of the platinum group metals, early-late heterobimetallic compounds containing halide bridges are rare.¹² Starting from the chloro-bridged complex $[\text{Rh}(\mu\text{-Cl})(\text{nbd})]_2$, Cano and co-workers have prepared $[(\text{CO})_3\text{M}(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})\text{Rh}(\text{nbd})]$ ($\text{M} = \text{Mo}, \text{W}$), the molybdenum complex of which shows a Mo-Rh distance of 2.945 Å (see Figure 27).¹⁵⁹

Early transition metal complexes containing alkoxide ligands are well-known. Although these ligands are usually terminally bound, alkoxide-bridged heterobimetallic species have also been described. Reaction of CuCl_2 with the alkoxytitanate $[\text{Ti}_2(\text{O}^i\text{Pr})_9]^-$ results in the formation of $[(^i\text{PrO})_4\text{Ti}_2(\mu^2\text{-O}^i\text{Pr})_3(\mu^3\text{-O}^i\text{Pr})_2\text{CuCl}]$ (see Figure 28).¹⁶⁰ Similarly, the anionic niobium or tantalum alkoxide complexes $[\text{M}(\text{O}^i\text{Pr})_6]^-$ react with FeCl_3 to give $\text{Fe}[\text{M}(\text{O}^i\text{Pr})_6]_3$: the authors have suggested that one-third of the isopropoxide ligands are in bridging positions.¹⁶¹

Hydrozirconation of the η^2 -phosphaalkyne complex $[\text{Pt}(\text{dpppe})(\eta^2\text{-}^t\text{BuC}\equiv\text{P})]$ leads to the complex $[\text{Cp}_2\text{ClZr}(\mu\text{-}\eta^1\text{Zr}, \eta^2\text{Pt-P}=\text{CH}^t\text{Bu})\text{Pt}(\text{dpppe})]$, in which the resulting phosphaalkene is bonded to zirconium through phosphorus in a manner similar to that of a terminal phosphido ligand.¹⁶²

As has been noted above (section III.C.3), terminal phosphido complexes of early transition metals can act in many ways similar to tertiary organophosphine ligands. Challet and co-workers have oxidized the niobium and tantalum phosphido complexes $[\text{Cp}_2\text{M}(\text{CO})(\text{PR}_2)]$ ($\text{R} = \text{Me}, \text{Ph}$) with elemental sulfur to produce $[\text{Cp}_2\text{M}(\text{CO})(\text{PSR}_2)]$, the equivalent of a phos-

Table 8. Indenyl-Bridged Heterobimetallic Compounds^a

	$r(\text{M}-\text{M})/\text{\AA}$	ref
$\text{syn}/\text{anti}-[(\text{OC})_3\text{Cr}(\mu\text{-C}_9\text{R}_7)\text{Rh}(\text{CO})_2]$ ($\text{R} = \text{H}, \text{Me}$)	3.077(1) (<i>syn</i> , $\text{R} = \text{H}$) nr (<i>anti</i> , $\text{R} = \text{Me}$)	150, 152, 153, 156
$\text{syn}-[(\text{OC})_3\text{Cr}(\mu\text{-C}_9\text{H}_7)\text{RhL}]$ ($\text{L} = \text{cod}, \text{nbd}$)	3.27 ($\text{L} = \text{cod}$) 3.181(1) ($\text{L} = \text{nbd}$)	150, 152, 154
$\text{anti}-[(\text{OC})_3\text{Cr}(\mu\text{-C}_9\text{R}_7)\text{RhL}]$ ($\text{R} = \text{H}, \text{Me}; \text{L} = \text{cod}, \text{nbd}$)	nr ($\text{R} = \text{Me}; \text{L} = \text{cod}$) nr ($\text{R} = \text{H}; \text{L} = \text{nbd}$)	153, 155, 156
$[(\text{OC})_3\text{Cr}(\mu\text{-C}_9\text{H}_5\text{R}^1\text{R}^3)\text{Rh}(\text{cod})]$ ($\text{R}^1, \text{R}^3 = \text{H}, \text{Me}, \text{Ph}$. $\text{R}^1 = \text{Me}, \text{Ph}; \text{R}^3 = \text{H}$)		157
$[(\text{OC})_3\text{Cr}(\mu\text{-C}_9\text{Me}_7)\text{Rh}(\text{CO})(\text{MeO}_2\text{CHC}=\text{CHCO}_2\text{Me})]$	nr	273
$\text{syn}-[(\text{OC})_3\text{Cr}(\mu\text{-C}_9\text{H}_7)\text{Ir}(\text{CO})_2]$	3.068(3)	158
$\text{anti}-[(\text{OC})_3\text{Cr}(\mu\text{-C}_9\text{H}_7)\text{Ir}(\text{cod})]$	nr	158
$\text{anti}-[(\text{OC})_3\text{Cr}(\mu\text{-C}_9\text{H}_7)\text{Ir}(\text{con})_2]$		158
$[(\text{OC})_3\text{Cr}(\mu\text{-C}_9\text{H}_7)\text{Ir}(\text{CO})_4]$		158
$[(\text{OC})_3\text{Cr}(\mu\text{-C}_9\text{H}_7)\text{Ir}(\text{CO})_3]_2$		158

^a nr = not reported.

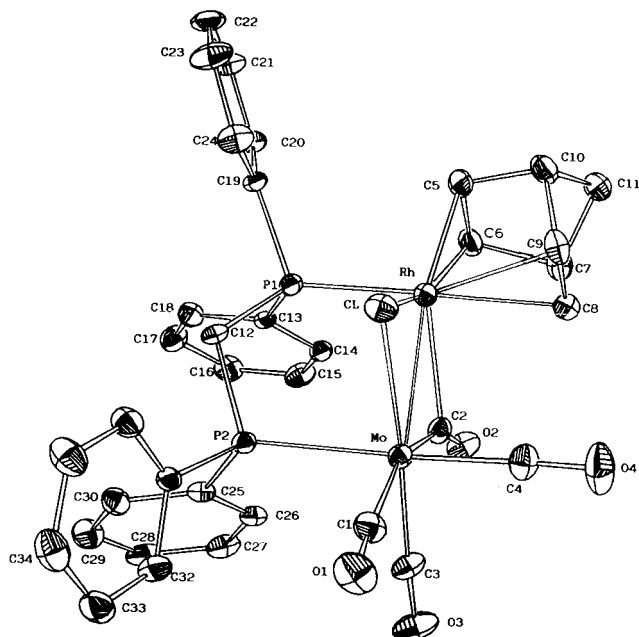


Figure 27. Crystal structure of $[(OC)_3Mo(\mu-Cl)(\mu-CO)(\mu-dppm)Rh(nbd)]$. Reprinted from ref 159. Copyright 1991 Elsevier Science Ltd.

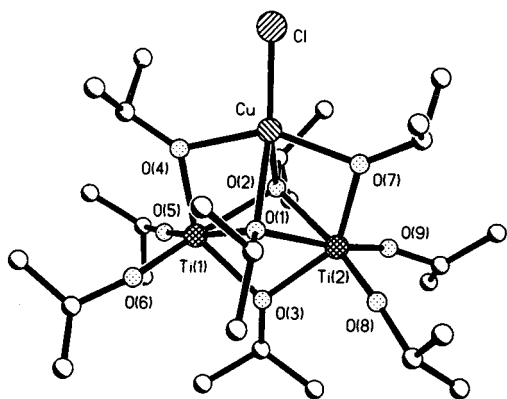


Figure 28. Crystal structure of $[(iPrO)_4Ti_2(\mu^2-iPrO)_3(\mu^3-iPrO)_2CuCl]$. Reprinted from ref 160. Copyright 1997 American Chemical Society.

phine sulfide.¹⁶³ The sulfur atom is a potential donor center, and was shown to coordinate to an $Fe(CO)_4$ fragment.

Although cyanide is well-known as a bridging ligand in the coordination chemistry of the late transition metals, there are few examples of cyanide-bridged heterobimetallic species. One example is $[(OC)_5M(\mu-CN)Cu(PPh_3)_3]$ ($M = Cr, W$), formed by the reaction of $[M(CN)(CO)_5]^-$ with $[Cu(MeCN)_4]^+$ in the presence of PPh_3 . The X-ray crystal structures of both complexes show the expected linear $MCNCu$ unit (see Figure 29). The tungsten complex shows an unexplained broadening of the cyanide ^{13}C NMR signal between $-80^\circ C$ and room temperature.¹⁶⁴

Treatment of $[Cl_2M(\mu-Cl)_2Cu(teta)]$ ($M = Ti, Zr$; $H_2teta =$ triethylenetetramine) with KBH_4 gives the borohydride-bridged species $[(H_3BH)_2M(\mu-BH_4)Cu(teta)]$.¹⁶⁵

The metallocarboxylate anions $[CpM'(CO)_2(CO)_2]^-$ ($M' = Fe, Ru$), obtained by reaction of CO_2 with $[CpM'(CO)_2]^-$, react with the group 4 metallocene

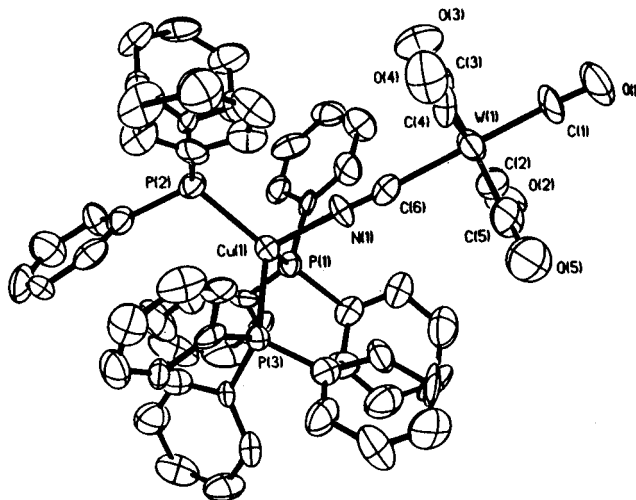


Figure 29. Crystal structure of $[(OC)_5W(\mu-CN)Cu(PPh_3)_3]$. Reprinted from ref 164. Copyright 1996 American Chemical Society.

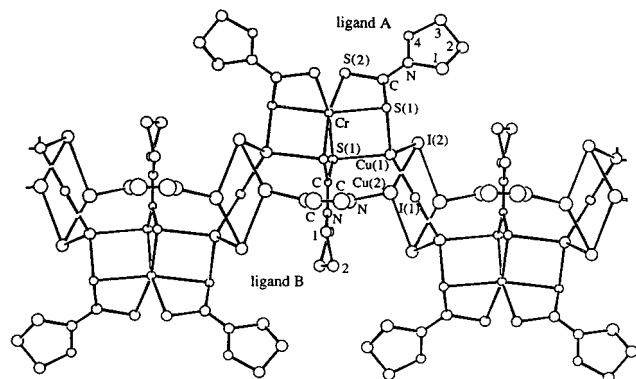


Figure 30. Crystal structure of the polymeric adduct $[Cr(S_2CNC_4H_8)_3] \cdot 3CuI$. Reprinted from ref 168. Copyright 1989 CSIRO Publishing.

dichlorides to give $[Cp_2CIM(\mu-CO_2-\kappa_M O, \kappa_M O', \kappa_M O'')M'(Cp)(CO)_2]$ ($M = Ti, Zr$): only the zirconium-ruthenium complex is stable at room temperature.¹⁶⁶ Reduction of this complex with $[Cp_2ZrHCl]$ affords $[Cp_2ClZr(\mu-OCH_2-\kappa_{Zr} O, \kappa_{Ru} C)RuCp(CO)_2]$: this unique bridging ligand is formally derived from the double deprotonation of methanol.¹⁶⁷

Although dithiocarbamates are not usually thought of as bridging ligands, copper(I) halide adducts of $[Cr(Et_2dtc)_3]$ have been obtained and characterized. The X-ray crystal structures show that the copper centers are each bound to the CrS_6 coordination sphere through two sulfur atoms (see Figure 30).¹⁶⁸

Reaction of the alkyldiene-bridged compounds $[(OC)_2CpM(\mu-CAR)Fe(CO)_3]$ (see section III.E) with elemental sulfur or selenium affords the unusual bridged species $[(OC)_2CpM(\mu-ECAR)Fe(CO)_3]$ ($M = Cr, Mo, W$; $E = S, Se$; $Ar = C_6H_3Me_2-2,6$). The bridging ligand, formally derived from the deprotonation of a chalcogenoaldehyde, donates no fewer than seven electrons to the system.^{169,170}

Gruselle and co-workers have examined the stabilization of carbenium cations in early-late bimetallic systems. A ferrocenyl-substituted propargyl alcohol can be bound to a $Mo_2Cp_2(CO)_4$ unit through the carbon-carbon triple bond. Subsequent removal of the hydroxyl group following protonation leads to

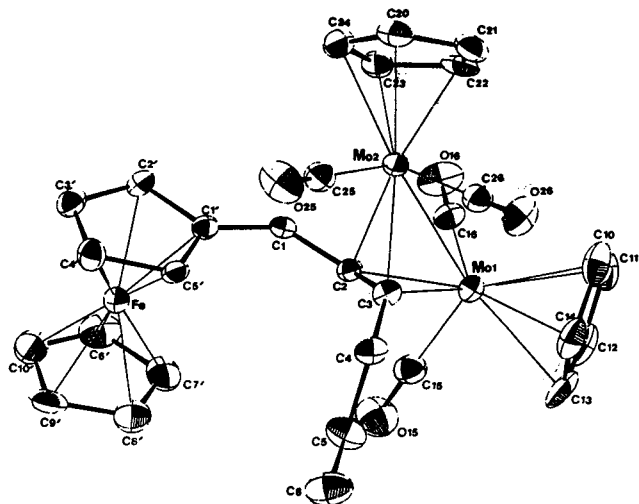


Figure 31. Crystal structure of $[(OC)_4Cp_2Mo_2(\mu-C_5H_{11}C\equiv CCHC_5H_4)FeCp]^+$. Reprinted from ref 172. Copyright 1992 American Chemical Society.

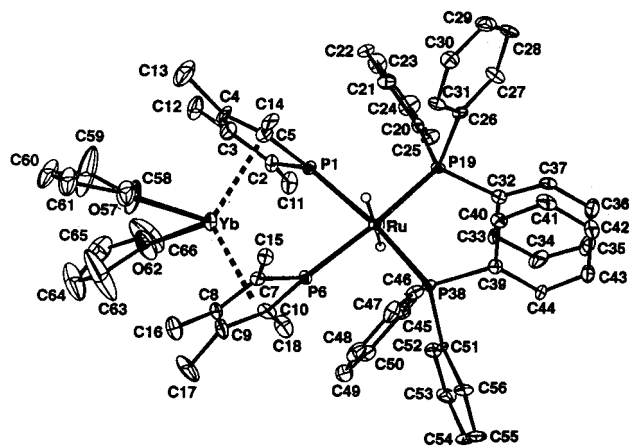


Figure 32. Crystal structure of $[(thf)_2Yb(\mu-C_4Me_4P)_2RuH_2(PPh_3)_2]$. Reprinted from ref 175. Copyright 1996 American Chemical Society.

organometallic carbenium ions, e.g., $[(OC)_4Cp_2Mo_2(\mu-C_5H_{11}C\equiv CCH^+C_5H_4)FeCp]$ (see Figure 31). Crystallographic and NMR studies indicate that the positive charge is stabilized by both the ferrocenyl iron center and the dimolybdenum moiety.^{171–173} In a similar manner, a carbenium cation can be stabilized by a $(OC)_2CpMoCo(CO)_3$ group bound to a triple

Table 9. Imido-Bridged Heterobimetallic Compounds^a

	$r(M-M)/\text{\AA}$	ref
$[Cp_2Zr(\mu-N^tBu)IrCp^*]$	2.598(2)	8, 178–180
$[Cp_2(RO)Zr(\mu-N^tBu)(\mu-H)IrCp^*]$ (R = ^t Bu, Tol, CMe=CH ₂)	3.020(1) (R = Tol)	179, 180
$[Cp_2(TolHN)Zr(\mu-N^tBu)(\mu-H)IrCp^*]$	2.977(1)	179, 180
$[Cp_2Zr(H)(STol)(\mu-N^tBu)IrCp^*]$		179, 180
$[Cp_2Zr(\mu-O)(\mu-N^tBu)IrCp^*]$		178
$[Cp_2Zr(\mu-S)(\mu-N^tBu)IrCp^*]$		8, 178, 180
$[Cp_2HZr(\mu-N^tBu)(\mu-H)IrCp^*]$	2.968(1)	8, 180
$[Cp_2(PhMeHSi)Zr(\mu-N^tBu)(\mu-H)IrCp^*]$		180
$[Cp(^tBuO)(TfO)Zr(\mu-N^tBu)(\mu-H)IrCp^*]$		179
$[Cp_2(^tBuO)Zr(\mu-N^tBu)(\mu-H)IrCp^*(PMe_3)]$		179
$[Cp_2Zr(\mu-C_3H_4)(\mu-N^tBu)IrCp^*]$		8
$[Cp_2Zr(\mu-N^tBu)\{\mu-OC(=O)\}IrCp^*]$	nr	8
$[Cp_2\{HC(=O)O\}Zr(\mu-N^tBu)(\mu-H)IrCp^*]$	nr	8
$[Cp_2Zr(\mu-NMe)\{\mu-N^tBuC(=O)\}IrCp^*]$	nr	8
$[Cp_2Zr(\mu-N^tBu)_2IrCp^*]$	2.9160(6)	181

^a nr = not reported.

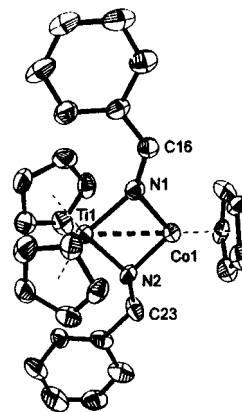


Figure 33. Crystal structure of $[Cp_2Ti(\mu-N=CHPh)_2CoCp]$. Reprinted from ref 177. Copyright 1998 American Chemical Society.

bond: these systems are prepared by the ligation of a $Co_2(CO)_6$ group to the triple bond followed by substitution with $[CpMo(CO)_3]^-$.¹⁷⁴

The tetramethylphosphole complexes $[(\eta^5-C_4PMe_4)_2-ZrCl_2]$, $[(\eta^5-C_4PMe_4)_2Yb(thf)_2]$, and $[Yb(\eta^5-C_4PMe_4)_2-(C_3N_2^iPr_2)]$ can act as bidentate phosphorus-donor ligands for ruthenium(II), displacing H_2 and PPh_3 from $[RuH_2(H_2)(PPh_3)_3]$ to form heterobimetallic complexes.^{175,176} The crystal structure of $[(thf)_2Yb(\mu-C_4PMe_4-\kappa_{Yb}C_4P(\eta^5),\kappa_{Ru}P)RuH_2(PPh_3)_2]$ has been determined (see Figure 32), and the decomposition of $[(C_3N_2^iPr_2)Yb(\mu-C_4PMe_4-\kappa_{Yb}C_4P(\eta^5),\kappa_{Ru}P)RuH_2(PPh_3)_2]$ in solution has been studied (see section V.N).

An alkylideneamido-bridged titanium–cobalt complex has been prepared by reaction of $[CpCo(C_2H_4)_2]$ with a titanium azine complex, itself formed by reaction of $PhHC=N-N=CHPh$ with $[Cp_2Ti(Me_3SiC\equiv CSiMe_3)]$. The X-ray crystal structure of the product, $[Cp_2Ti(\mu-N=CHPh)CoCp]$, has been determined (see Figure 33).¹⁷⁷

D. Compounds Containing Bidentate Bridging Ligands

1. Imido-Bridged Compounds

Many imido-bridged zirconium–iridium complexes (see Table 9) have been synthesized by the oxidative

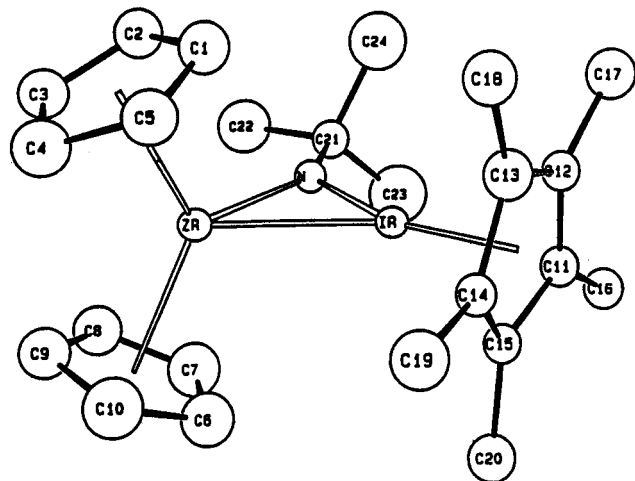


Figure 34. Crystal structure of $[\text{Cp}_2\text{Zr}(\mu\text{-N}^t\text{Bu})\text{IrCp}^*]$. Reprinted from ref 180. Copyright 1994 American Chemical Society.

addition of organic substrates to the zirconium–iridium bond of $[\text{Cp}_2\text{Zr}(\mu\text{-N}^t\text{Bu})\text{IrCp}^*]$. This complex is itself prepared by the reaction of the iridium nitrene $[\text{Cp}^*\text{Ir}=\text{N}^t\text{Bu}]$ with a source of “ Cp_2Zr ”. The Zr–Ir distance is very short (2.598 Å) and the Zr–N–Ir angle is quite acute (81.6°), as can be seen in Figure 34. The strained three-membered ring is relaxed following oxidative addition, leading to the introduction of a second bridging group and the disappearance of the metal–metal bond (see sections V.A and V.C).^{8,178–180} A bis(imido)-bridged compound, $[\text{Cp}_2\text{Zr}(\mu\text{-N}^t\text{Bu})_2\text{IrCp}^*]$, can be prepared by reaction of $[\text{Cp}^*\text{Ir}(\text{OCMe}_2\text{CMe}_2\text{O})]$ with an excess of $[\text{Cp}_2\text{Zr}(\text{N}^t\text{Bu})(\text{thf})]$.¹⁸¹

2. Oxo- and Sulfido-Bridged Compounds

The relatively hard osmium(VI) center of $[\text{Os}(\equiv\text{N})\text{R}_2\text{Cl}_2]^-$ ($\text{R} = \text{Me}, \text{CH}_2\text{SiMe}_3$) is able to accept a μ -oxo ligand from CrO_4^{2-} by substitution of chloride.¹⁸² The resulting anionic complex, $[\text{O}_2\text{Cr}(\mu\text{-O})_2\text{Os}(\equiv\text{N})\text{R}_2]^-$, reacts with dppe to give $[\text{O}_3\text{Cr}(\mu\text{-O})\text{Os}(\equiv\text{N})\text{R}_2(\text{dppe})]^-$, which has been crystallographically characterized.¹⁸³ A similar reaction with MoS_4^{2-} and WS_4^{2-} gives the corresponding sulfido-bridged complexes $[\text{S}_2\text{M}(\mu\text{-S})_2\text{Os}(\equiv\text{N})\text{R}_2]^-$ (see Figure 35).¹⁸⁴ The X-ray crystal structure of the tungsten–osmium complex shows a W–Os distance of 2.897 Å (Table 10). Use of the neutral osmium(VI) precursor $[\text{Os}(\equiv\text{N})(\text{CH}_2\text{SiMe}_3)_2\text{Cl}]_2$ in this case results in the neutral trinuclear

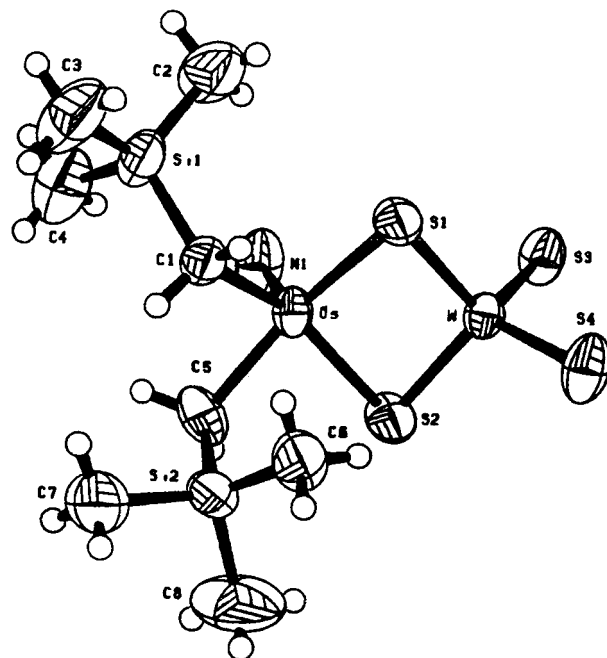


Figure 35. Crystal structure of $[\text{S}_2\text{W}(\mu\text{-S})_2\text{Os}(\equiv\text{N})(\text{CH}_2\text{SiMe}_3)_2]$. Reprinted from ref 184. Copyright 1993 American Chemical Society.

species $[\text{W}\{(\mu\text{-S})_2\text{Os}(\equiv\text{N})(\text{CH}_2\text{SiMe}_3)_2\}_2]$.¹⁸⁴ Addition of PPh_4Cl to this product leads to substitution of half the sulfido bridges, giving the dianion $[\text{S}_2\text{W}\{(\mu\text{-S})\text{Os}(\equiv\text{N})\text{Cl}(\text{CH}_2\text{SiMe}_3)_2\}_2]^{2-}$. Analogously, the reaction of MS_4^{2-} ($\text{M} = \text{Mo}, \text{W}$) to $[\text{PdCl}_2(\text{dppe})]$ gives $[\text{S}_2\text{M}(\mu\text{-S})_2\text{Pd}(\text{dppe})]$. The X-ray crystal structure of the tungsten–palladium compound shows a W–Pd distance of 2.89 Å.¹⁸⁵

An alternative strategy for the preparation of sulfido-bridged complexes is to start from the zirconocene hydrosulfide $[\text{Cp}^*_2\text{Zr}(\text{SH})_2]$. Reaction of this compound with $[\text{RhCl}_2(\text{CO})_2]^-$ gives $[\text{Cp}^*_2\text{Zr}(\mu\text{-S})_2\text{Rh}(\text{CO})_2]^-$, in which the X-ray crystal structure shows a Zr–Rh distance of 3.16 Å.¹⁸⁶

Reaction of $[\text{Cp}_2\text{Ti}(\text{SH})_2]$ with $[\text{Rh}(\text{OMe})(\text{tfbb})]_2$ (tfbb = tetrafluorobenzobarrelene) leads to the loss of a cyclopentadienyl ligand from the titanium and the formation of the tetranuclear cluster $[\text{CpTi}(\mu_3\text{-S})_3\{\text{Rh}(\text{tfbb})\}_3]$, the X-ray crystal structure of which has been determined (see Figure 36).¹⁸⁷

The molybdenum–cobalt cluster $[\text{Mo}_2\text{Co}_2\text{Cp}_2(\mu_3\text{-S})_3(\text{CO})_4]$ reacts with diphosphine (dppm, dppe, dmpe) to give $[\text{Mo}_2\text{Co}_2\text{Cp}_2(\mu_3\text{-S})_3(\text{CO})_2(\text{diphos})]$. When dmpe

Table 10. Oxo- and Sulfido-Bridged Heterobimetallic Compounds^a

	$r(\text{M}-\text{M}')/\text{\AA}$	ref
$[\text{CpTi}(\mu_3\text{-S})_3\{\text{Rh}(\text{tfbb})\}_3]$	2.919(3), 2.940(3), 2.912(3)	187
$[\text{CpTi}(\mu_3\text{-S})_3\{\text{Rh}(\text{CO})\text{L}\}_3]$ ($\text{L} = \text{CO}, \text{PPh}_3$)		187
$[\text{Cp}^*_2\text{Zr}(\mu\text{-S})_2\text{Rh}(\text{CO})_2]^-$	3.161(3)	186
$[\text{Cp}_2\text{Zr}(\mu\text{-N}^t\text{Bu})(\mu\text{-O})\text{IrCp}^*]$		178
$[\text{Cp}_2\text{Zr}(\mu\text{-N}^t\text{Bu})(\mu\text{-S})\text{IrCp}^*]$	2.968(1)	8, 178, 180
$[\text{O}_2\text{Cr}(\mu\text{-O})_2\text{Os}(\equiv\text{N})\text{R}_2]$ ($\text{R} = \text{Me}, \text{CH}_2\text{SiMe}_3$)		182, 183
$[\text{O}_3\text{Cr}(\mu\text{-O})\text{Os}(\equiv\text{N})(\text{CH}_2\text{SiMe}_3)_2(\text{dppe})]$	nr	183
$[\text{S}_2\text{M}(\mu\text{-S})_2\text{Os}(\equiv\text{N})(\text{CH}_2\text{SiMe}_3)_2]$ ($\text{M} = \text{Mo}, \text{W}$)	2.8970(5) ($\text{M} = \text{W}$)	184
$[\text{S}_2\text{W}(\mu\text{-S})_2\text{Os}(\equiv\text{N})\text{Me}_2]$		184
$[\text{W}\{(\mu\text{-S})_2\text{Os}(\equiv\text{N})(\text{CH}_2\text{SiMe}_3)_2\}_2]$	2.8372(4), 2.8373(4)	184
$[\text{S}_2\text{M}(\mu\text{-S})_2\text{Pd}(\text{dppe})]$ ($\text{M} = \text{Mo}, \text{W}$)	2.887(2) ($\text{M} = \text{Mo}$)	185
$[\text{Cp}(\text{O}=\text{W}(\mu\text{-O})(\mu\text{-TolCC}_6\text{H}_4\text{CH}_2\text{NMe}_2)\text{PdCl}]$	2.6753(4)	201

^a nr = not reported.

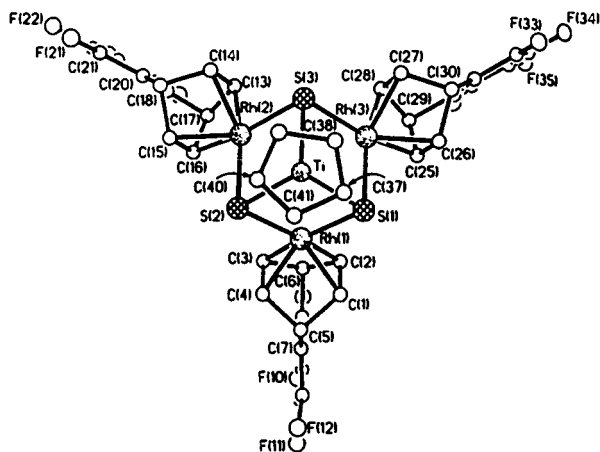


Figure 36. Crystal structure of $[\text{CpTi}(\mu_3\text{-S})_3\{\text{Rh}(\text{tfbb})\}_3]$. Reprinted from ref 187. Copyright 1996 Elsevier Science Ltd.

is used, the reaction can continue to give $[\text{Mo}_2\text{Co}_2\text{Cp}_2(\mu_3\text{-S})_3(\mu_3\text{-CO})(\text{dmpe})_2]$, in which the triply bridging carbonyl has a stretching frequency of 1615 cm^{-1} . This latter complex reacts with dichloromethane to generate a μ_3 -methylidyne species, $[\text{Mo}_2\text{Co}_2\text{Cp}_2(\mu_3\text{-S})_3(\mu_3\text{-CH})(\text{dmpe})_2]$ (see Figure 37).¹⁸⁸

3. Alkylidene-Bridged Compounds

A general method for the preparation of methylene-bridged heterobimetallic complexes of titanium is the reaction of the late transition metal precursor with

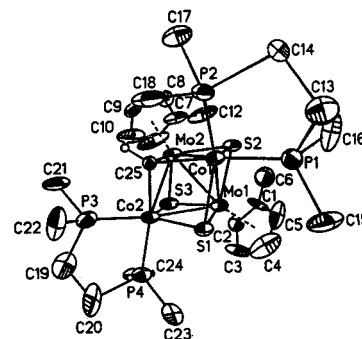


Figure 37. Crystal structure of $[\text{Mo}_2\text{Co}_2\text{Cp}_2(\mu_3\text{-CH})(\mu_3\text{-S})_3(\text{dmpe})_2]$. Reprinted from ref 188. Copyright 1997 American Chemical Society.

the titanocyclobutane, with concomitant elimination of isobutene. This approach has been used to prepare complexes of rhodium, iridium, palladium, platinum, and gold of general formula $[\text{Cp}_2\text{Ti}(\mu\text{-CH}_2)(\mu\text{-Cl})\text{ML}_n]$.^{189,190}

Among the different carbon-centered bridges, the μ -phenyl ligand in $[\text{Cp}_2\text{Ti}(\mu\text{-C}_6\text{H}_4\text{X})(\mu\text{-CH}_2)\text{Rh}(\text{cod})]$ is particularly notable as a three-center two-electron bridge in a relatively electron-poor system. The X-ray crystal structure of the $\text{X} = \text{NMe}_2$ complex shows clearly that only one carbon atom is involved in the bridge: the Ti–Rh distance is 2.827 \AA (Table 11).¹⁹¹ Methylene-bridged titanium–platinum complexes $[\text{Cp}_2\text{Ti}(\mu\text{-CH}_2)(\mu\text{-Cl})\text{PtMeL}]$ ($\text{L} = \text{SMe}_2, \text{PMe}_3, \text{PMe}_2\text{-Ph}, \text{PMePh}_2$) have been prepared by the reaction of

Table 11. Alkylidene-Bridged Heterobimetallic Compounds^a

	$r(\text{M}-\text{M}')/\text{\AA}$	ref
$[\text{Cp}_2\text{Ti}(\mu\text{-CH}_2)(\mu\text{-X})\text{Rh}(\text{cod})]$ ($\text{X} = \text{Cl}, \text{OMe}$)	2.986(2) ($\text{X} = \text{Cl}$)	189
$[\text{Cp}_2\text{Ti}(\mu\text{-CH}_2)(\mu\text{-Cl})\text{RhL}(\text{SMe}_2)]$ ($\text{L} = \text{CO}, \text{C}_2\text{H}_4$)		189
$[\text{Cp}_2\text{Ti}(\mu\text{-CH}_2)(\mu\text{-C}_6\text{H}_4\text{R})\text{Rh}(\text{cod})]$ ($\text{R} = \text{H}, \text{NMe}_2, \text{OMe}$)	2.827(1) ($\text{R} = \text{NMe}_2$)	191
$[\text{Cp}_2\text{Ti}(\mu\text{-CH}_2)(\mu\text{-Cl})\text{Ir}(\text{cod})]$		189
$[\text{Cp}_2\text{Ti}(\mu\text{-CH}_2)(\mu\text{-Cl})\text{Pd}(\text{C}_3\text{H}_4\text{Me})]$		189
$[\text{Cp}_2\text{Ti}(\mu\text{-CH}_2)(\mu\text{-Cl})\text{PdMe}(\text{PMe}_3)]$		190
$[\text{Cp}_2\text{Ti}(\mu\text{-Cl})(\mu\text{-CH}_2)\text{PtMeL}]$ ($\text{L} = \text{PMe}_3, \text{PMe}_2\text{Ph}, \text{PMePh}_2, \text{SMe}_2$)	2.962(2) ($\text{L} = \text{PMe}_2\text{Ph}$)	189, 190
$[\text{Cp}_2\text{Ti}(\mu\text{-CH}_2)(\mu\text{-CH}_3)\text{PtMe}(\text{PMe}_2\text{Ph})]$	2.776(1)	190
$[\text{ClCp}_2\text{Ti}(\mu\text{-CH}_2)\text{PtMeL}_2]$ ($\text{L} = \text{PMe}_2\text{Ph}, \text{PMePh}_2$)		190
$[\text{Cp}_2\text{Ti}(\mu\text{-CH}_2)(\mu\text{-Cl})\text{Au}(\text{PPh}_3)]$		189
$[\text{Cp}_2\text{Ta}(\mu\text{-CH}_2)_2\text{CoCp}]$	2.708	192, 196
$[\text{Cp}_2\text{Ta}(\mu\text{-CH}_2)_2\text{CoCp}(\text{SR})]$ ($\text{R} = \text{Ph}, \text{Tol}, \text{C}_6\text{H}_3\text{Me}_2, \text{C}_6\text{H}_4\text{OMe}, \text{C}_6\text{H}_4\text{CF}_3$)	2.8005(8) ($\text{R} = \text{C}_6\text{H}_3\text{Me}_2$)	196, 268
$[\text{Cp}_2\text{Ta}(\mu\text{-CH}_2)_2\text{CoCpL}]^+$ ($\text{L} = \text{MeCN}, \text{PMe}_3, \text{CO}$)		192
$[\text{Cp}_2\text{Ta}(\mu\text{-CH}_2)_2\text{M}(\text{CO})\text{L}]$ ($\text{M} = \text{Rh}, \text{Ir}; \text{L} = \text{CO}, \text{PPh}_3$)		262
$[\text{Cp}_2\text{Ta}(\mu\text{-CH}_2)_2\text{Ir}(\text{CO})_2]$		193, 195, 261–263
$[(\eta^5\text{-C}_9\text{H}_7)\text{CpTa}(\mu\text{-CH}_2)_2\text{Ir}(\text{CO})_2]$	2.858(1)	193
$[\text{Cp}_2\text{Ta}(\mu\text{-CH}_2)_2\text{IrH}(\text{SiEt}_3)(\text{CO})_2]$		261, 263
$[\text{Cp}_2\text{Ta}(\mu\text{-CH}_2)_2\text{IrCp}^*\text{X}]$ ($\text{X} = \text{H}, \text{Cl}, \text{I}, \text{Me}$)	2.776(1) ($\text{X} = \text{H}$)	195
$[\text{Cp}_2\text{Ta}(\mu\text{-CH}_2)_2\text{Pd}(\text{C}_5\text{R}_5)]$ ($\text{R} = \text{H}, \text{Me}$)		194
$[\text{Cp}_2\text{Ta}(\mu\text{-CH}_2)_2\text{PdClL}]$ ($\text{L} = \text{PMe}_3, \text{P}(\text{OMe})_3$)		194
$[\text{Cp}_2\text{Ta}(\mu\text{-CH}_2)_2\text{PdL}_2]^+$ ($\text{L} = \text{PMe}_3, \text{P}(\text{OMe})_3$)		194
$[\text{Cp}_2\text{Ta}(\mu\text{-CH}_2)_2\text{Pd}(\text{dmpe})]^+$	2.832(1), 2.829(2) ^b	194
$[\text{Cp}_2\text{Ta}(\mu\text{-CH}_2)_2\text{Pd}(\text{CH}_2\text{CN})\{\text{P}(\text{OMe})_3\}]$		194
$[\text{Cp}_2\text{MeTa}(\mu\text{-CH}_2)\text{Pt}(\text{PMe}_3)_2]$	nr	197
$[\text{Cp}_2\text{Ta}(\mu\text{-CH}_2)_2\text{PtH}(\text{PMe}_3)]$	nr	197
$[(\text{OC})_2\text{CpM}(\mu\text{-CH}_2)(\mu\text{-CO})\text{NiCp}^*]$ ($\text{M} = \text{Mo}, \text{W}$)	2.5689(6) ($\text{M} = \text{W}$)	202
$[(\text{OC})\text{CpM}(\mu\text{-RCC}_6\text{H}_4\text{CH}_2\text{Y})(\mu\text{-CO})\text{PdX}]$ ($\text{M} = \text{Mo}, \text{W}; \text{R} = \text{Tol}, \text{C}_5\text{H}_7, \text{C}_6\text{H}_4\text{tBu}, \text{C}_6\text{H}_3\text{Me}_2; \text{Y} = \text{NMe}_2, \text{SMe}, \text{C}_5\text{H}_4\text{N}; \text{X} = \text{Cl}, \text{I}$)		199
$[(\text{OC})\text{CpM}(\mu\text{-TolCC}_6\text{H}_4\text{C}_6\text{H}_4\text{Y})(\mu\text{-CO})\text{PdCl}]$ ($\text{M} = \text{Mo}, \text{W}; \text{Y} = \text{NMe}_2, \text{SMe}$)	2.6973(3) ($\text{M} = \text{W}; \text{Y} = \text{SMe}$)	199
$[(\text{tBuNC})_2\text{CpMo}(\mu\text{-TolCC}_6\text{H}_4\text{CH}_2\text{NMe}_2)(\mu\text{-CO})\text{PdI}]$	2.692(2)	200
$[\text{Cp}(\text{O}=\text{W})(\mu\text{-TolCC}_6\text{H}_4\text{CH}_2\text{NMe}_2)(\mu\text{-CO})\text{PdCl}]$	2.6939(6)	201
$[\text{Cp}(\text{O}=\text{W})(\mu\text{-TolCC}_6\text{H}_4\text{CH}_2\text{NMe}_2)(\mu\text{-O})\text{PdCl}]$	2.6753(4)	201

^a nr = not reported. ^b Two distinct structural determinations, with different anions.

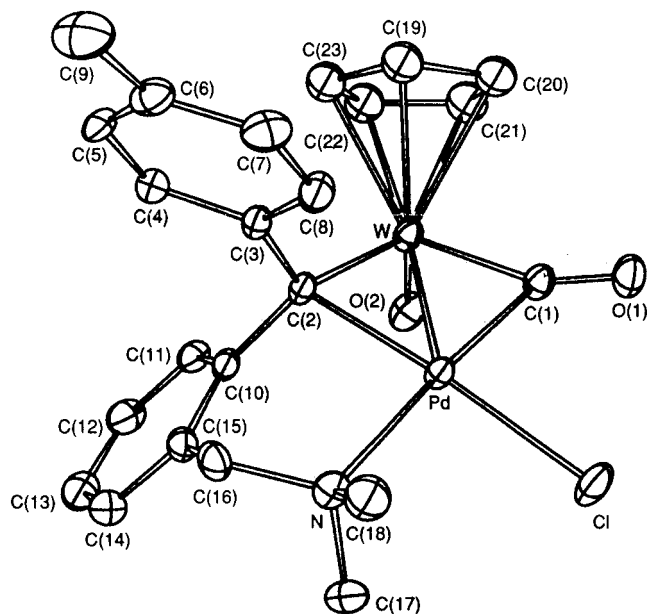


Figure 38. Crystal structure of $[\text{Cp}(\text{O}=\text{W})(\mu\text{-CTolC}_6\text{H}_4\text{CH}_2\text{NMe}_2)(\mu\text{-CO})\text{PdCl}]$. Reprinted from ref 201. Copyright 1997 Royal Society of Chemistry.

$[\text{PtClMe}(\text{SMe}_2)_2]$ with the titanocyclobutane $[\text{Cp}_2\text{Ti}\{(\text{CH}_2)_2\text{CMe}_2\}]$ and subsequent substitution of phosphine for dimethyl sulfide. Substitution of the chloro bridge with MeMgBr affords the unusual bridging methyl complexes $[\text{Cp}_2\text{Ti}(\mu\text{-CH}_2)(\mu\text{-CH}_3)\text{PtMe}(\text{PR}_3)]$. Both series of complexes have been crystallographically characterized.¹⁹⁰

Reaction of the terminal methylene complex $[\text{Cp}_2\text{-TaMe}(\text{CH}_2)]$ with the cobalt precursor $[\text{CpCo}(\text{C}_2\text{H}_4)_2]$ leads to the paramagnetic 33-electron system $[\text{Cp}_2\text{-Ta}(\mu\text{-CH}_2)_2\text{CoCp}]$. The X-ray crystal structure of this complex shows a Ta–Co distance of only 2.702 Å, while EPR studies are consistent with the unpaired electron being localized on the cobalt center.¹⁹² A similar procedure has been used to prepare heterobimetallic tantalum complexes of rhodium, iridium, palladium, and platinum:^{193–195} the reactivity of these complexes has been extensively studied (see sections V.C, VI.A, VI.G, and VI.H). $[\text{Cp}_2\text{Ta}(\mu\text{-CH}_2)_2\text{CoCp}]$ can be oxidized by Cp_2Fe^+ in the presence of a neutral donor ligand to give $[\text{Cp}_2\text{Ta}(\mu\text{-CH}_2)_2\text{CoCpL}]^+$ ($\text{L} = \text{MeCN}, \text{PMe}_3, \text{CO}$). It also reacts with organic disulfides to give $[\text{Cp}_2\text{Ta}(\mu\text{-CH}_2)_2\text{CoCp}(\text{SR})]$ ($\text{R} = \text{Ph}, \text{Tol}, \text{C}_6\text{H}_4\text{OMe}, \text{C}_6\text{H}_4\text{CF}_3, \text{C}_6\text{H}_4\text{Cl}, \text{C}_6\text{H}_3\text{Me}_2$), the crystal structure of the $\text{R} = \text{C}_6\text{H}_3\text{Me}_2$ complex of which has been determined.¹⁹⁶

In a similar manner, $[\text{Cp}_2\text{Ta}(\text{CH}_2)(\text{CH}_3)]$ reacts with $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PMe}_3)_2]$ to produce $[\text{Cp}_2\text{MeTa}(\mu\text{-CH}_2)\text{-Pt}(\text{PMe}_3)_2]$, which has been crystallographically characterized. This decomposes in a matter of hours in benzene solution at 40 °C to give an equimolar mixture of starting material and $[\text{Cp}_2\text{Ta}(\mu\text{-CH}_2)_2\text{PtH}(\text{PMe}_3)]$.¹⁹⁷

An insertion reaction between the cyclopalladated compounds $[\text{Pd}(\text{C}_6\text{H}_4\text{CH}_2\text{X})(\mu\text{-Cl})_2]$ ($\text{X} = \text{NMe}_2, \text{SMe}$) and the carbynes (metallaalkynes) $[\text{M}(\equiv\text{CAr})\text{Cp}(\text{CO})_2]$ ($\text{M} = \text{Mo}, \text{W}$; $\text{Ar} = \text{C}_6\text{H}_4\text{Me}, \text{C}_6\text{H}_4\text{tBu}, \text{C}_6\text{H}_3\text{-Me}_2, \text{C}_5\text{H}_7$) leads to the alkylidene-bridged heterobimetallic species $[(\text{OC})\text{CpM}(\mu\text{-CO})(\mu\text{-CArC}_6\text{H}_4\text{CH}_2\text{X-}\kappa_{\text{M}}\text{C}, \kappa_{\text{Pd}}\text{C}, \kappa_{\text{Pd}}\text{X})\text{PdCl}]$.^{198,199} Multinuclear NMR studies

of these compounds indicate the presence of an η^2 -interaction between the aromatic ring attached to the alkylidene carbon and the early metal center.²⁰⁰ Oxidation of these complexes with trimethylamine *N*-oxide has afforded the complexes $[\text{Cp}(\text{O}=\text{W})(\mu\text{-CTolC}_6\text{H}_4\text{CH}_2\text{NMe}_2)(\mu\text{-CO})\text{PdCl}]$ (see Figure 38) and $[\text{Cp}(\text{O}=\text{W})(\mu\text{-O})(\mu\text{-CTolC}_6\text{H}_4\text{CH}_2\text{NMe}_2)\text{PdCl}]$ in low yields. The X-ray crystal structures of both these complexes, which retain the starting μ -alkylidene framework, have been solved.²⁰¹

Finally, Chetcuti et al. have prepared and crystallographically characterized a methylene-bridged tungsten–nickel compound, $[(\text{OC})_2\text{CpW}(\mu\text{-CH}_2)(\mu\text{-CO})\text{-NiCp}^*]$, by the reaction of diazomethane with $[\text{CpW}(\mu\text{-CO})_3\text{NiCp}^*]$.²⁰²

4. CpX-Type Bridges

In addition to the well-known phosphino-substituted cyclopentadienyl ligands, certain groups have examined the possibility of using cyclopentadienyl ligands substituted with anionic donor groups. Thus, reactions of $[(\text{NaO}_2\text{CC}_5\text{H}_4)\text{FeBz}(\text{CO})_2]$ with $[\text{Cp}_2\text{MCl}_2]$ ($\text{M} = \text{Ti}, \text{Zr}$) lead to the complexes $[\text{Cp}_2\text{M}\{(\mu\text{-O}_2\text{CC}_5\text{H}_4)\text{-FeBz}(\text{CO})_2\}_2]$, the X-ray crystal structure of the titanium complex of which has been obtained.²⁰³ Similarly, the reaction of $[\text{CpFe}(\text{C}_5\text{H}_4\text{C}\equiv\text{CLi})]$ with $[(\text{C}_5\text{H}_4\text{SiMe}_3)_2\text{TiCl}_2]$ affords the trinuclear complex $[(\text{C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}\{(\mu\text{-C}\equiv\text{CC}_5\text{H}_4)\text{FeCp}\}_2]$ (see Figure 39).²⁰⁴ This metallaalkyne complex reacts with $\text{Ni}(\text{CO})_4$

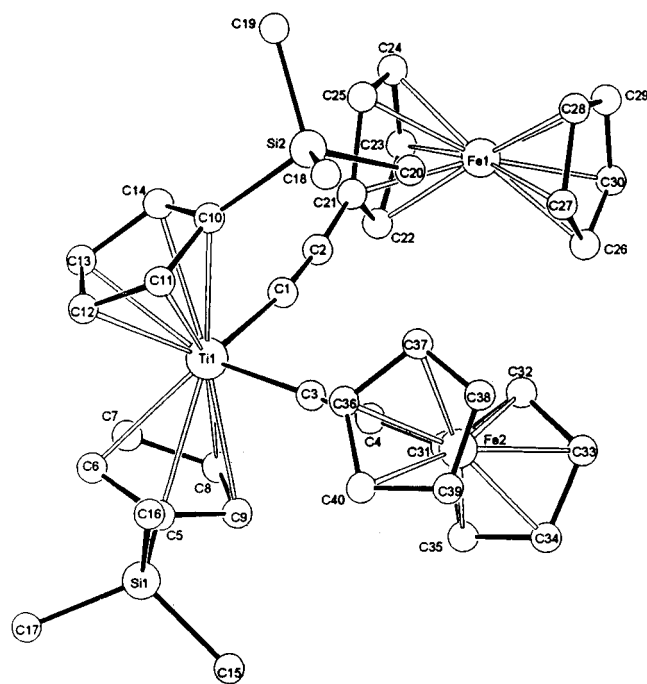


Figure 39. Crystal structure of $[(\text{C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}\{(\mu\text{-C}\equiv\text{CC}_5\text{H}_4)\text{FeCp}\}_2]$. Reprinted from ref 204. Copyright 1998 American Chemical Society.

to give a pincer complex, $[(\text{C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}\{(\mu\text{-C}\equiv\text{CC}_5\text{H}_4)\text{FeCp}\}_2\text{Ni}(\text{CO})]$.²⁰⁴ Complexes of the type $[\text{Tp}^*\text{MCl}(\text{NO})\text{X}]$ ($\text{M} = \text{Mo}, \text{W}$), in which X is an anionic phenolato- or anilido-substituted ferrocene, $[\text{CpFe}(\text{C}_5\text{H}_4\text{C}_6\text{H}_4\text{O})]^-$ or $[\text{CpFe}(\text{C}_5\text{H}_4\text{C}_6\text{H}_4\text{NH})]^-$, have been prepared, and their potential for nonlinear optical applications has been examined.²⁰⁵

5. Compounds Bridged by an Alkyl Chain

A considerable amount of work has been carried out on bimetallic complexes in which the metal centers are linked by a carbon chain, saturated or unsaturated.²⁰⁶ For example, a chain of three methylene groups separates the molybdenum and iron centers in $[(OC)_3CpMo(\mu-C_3H_6)FeCp(CO)_2]$.²⁰⁷ This complex reacts with Ph_3C^+ with hydride abstraction from the chain (see section V.J): the structure of the product is uncertain, but may be similar to that of the homobimetallic analogue, $[(OC)_2CpFe(\mu-C_3H_5)FeCp(CO)_2]^+$, in which there is an interaction between the central atom of the chain and the two metal centers. The related series of compounds $[(OC)_3CpM\{\mu-(CH_2)_n\}FeCp^*(CO)_2]$ ($M = Mo, W; n = 3-6$) has been prepared by the reaction of $[CpM(CO)_3]^-$ with $[Cp^*Fe(CO)_2\{\mu-(CH_2)_nI\}]$.²⁰⁸

The hydrozirconation of ruthenium metalloalkynes or metalloalkenes with Schwartz's reagent has been used to prepare the carbon-bridged zirconium–ruthenium complexes $[Cp_2ClZr(\mu-CH=CH)RuCp(PMe_3)_2]$ (see Figure 40) and $[Cp_2ClZr(\mu-CH_2CH_2)-$

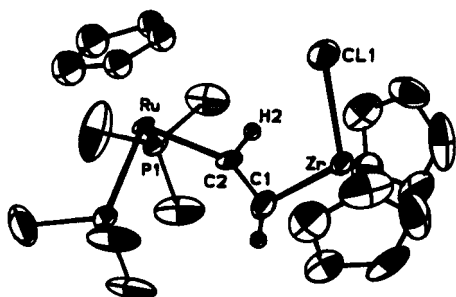


Figure 40. Crystal structure of $[Cp_2ClZr(\mu-CH=CH)RuCp(PMe_3)_2]$. Reprinted from ref 210. Copyright 1991 American Chemical Society.

$RuCp(PMe_3)_2]$. These complexes have been crystallographically characterized, and both show agostic interactions between the zirconium center and the β -CH bond of the bridge.^{209,210} The reaction of $[CpRu(C\equiv CH)(PMe_3)_2]$ with $[Cp_2ZrCl(NMe_2)]$ leads to elimination of dimethylamine, giving the heterodimetalloalkyne $[Cp_2ClZr(\mu-C\equiv C)RuCp(PMe_3)_2]$.²⁰⁹ Palladium-catalyzed metal–carbon coupling has also been used to prepare dimetalloalkynes, notably $[(OC)_3CpMo(\mu-C\equiv CC_4H_2SC\equiv C)Fe(indenyl)(CO)_2]$.²¹¹

Reaction of allene with $[(OC)Cp'Mo(\mu-CO)_2NiCp(CO)]$ gives the tris-allyl-bridged species $[(OC)_2Cp'Mo\{\mu-C_3H_4CH_2C(=CH_2)C_3H_4\}NiCp]$ (see Figure 41) in very low yield (see section V.H). The X-ray crystal

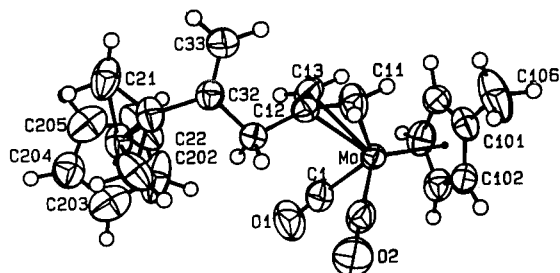


Figure 41. Crystal structure of $[(OC)_2Cp'Mo\{\mu-C_3H_4-CH_2C(=CH_2)C_3H_4\}NiCp]$. Reprinted from ref 212. Copyright 1991 American Chemical Society.

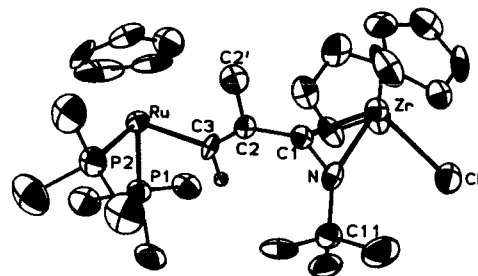


Figure 42. Crystal structure of $[Cp_2ClZr(\mu-^iBuN=CCMe=CH)RuCp(PMe_3)_2]$. Reprinted from ref 213. Copyright 1992 American Chemical Society.

structure shows that the two metals are far-separated from one another.²¹² Similar compounds bridged by iminoacyl ligands have been obtained from the reaction of isonitriles RNC ($R = Me, ^iBu$) with $[Cp_2ClZr(\mu-CH=CH)RuCp(PMe_3)_2]$, giving $[Cp_2ClZr(\mu-RN=CCH=CH-\kappa_{Zr}N, \kappa_{Zr}C, \kappa_{Ru}C')RuCp(PMe_3)_2]$ (see Figure 42).²¹³

6. Fulvalene and Related Bridges

The fulvalene ligand, two cyclopentadienyl rings linked by a single carbon–carbon bond, is an attractive proposition for holding two metal centers in close proximity to one another. The ligand is usually prepared from a cyclopentadienyl group already attached to a metal center. Hence, dilithioferrocene reacts with tetramethylcyclopentenone to afford the iron complex of tetramethylfulvalene, $[CpFe(C_5H_4C_5-Me_4H)]$. This will react with $[ZrCl_4(thf)_2]$ to give the heterobimetallic zirconium–iron complex. In this case, the two metal centers are in fact well separated from one another (4.448 Å).²¹⁴ Reaction of $[CpFe(C_5H_4C_5Me_4H)]$ with $[MCl(\eta^3-C_3H_5)(CO)_2(MeCN)_2]$ ($M = Mo, W$) leads to the fulvalene-bridged heterobimetallics $[(OC)_2(\eta^3-C_3H_5)M(\mu-C_5Me_4C_5H_4)FeCp]$, in which the two metal centers adopt a transoid configuration with respect to the planar fulvalene group.^{215,216} The cisoid configuration can be forced upon a tungsten–rhodium system, $[(OC)_3MeW(\mu-C_5H_4C_5H_4)RhAc(CO)]$, by photochemical removal of a carbonyl ligand with the concomitant formation of a metal–metal bond (Figure 43).²¹⁷ Heck coupling can also be used to link two metal-bound cyclopentadienyl groups, and molybdenum–iron and tungsten–iron complexes of the $C_5H_4C\equiv CC_5H_4^{2-}$ ligand have been prepared by this route.²¹⁸

Electrochemical coupling is a third option for the preparation of fulvalene-type systems. $[Fe(C_5H_4Br)-$

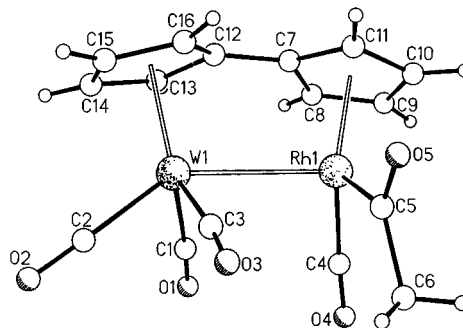


Figure 43. Crystal structure of $[(OC)_3W(\mu-C_5H_4C_5H_4)RhAc(CO)]$. Reprinted from ref 217. Copyright 1994 Elsevier Science Ltd.

(C₅H₄COMe)] can be reductively coupled to give [(MeCOC₅H₄)Fe(μ -C₅H₄C₅H₄)Fe(C₅H₄COMe)]: one of the iron centers can be reductively removed, and a second metal center attached to the fulvalene ligand.²¹⁹ It has been shown that the metal–metal bond in the fulvalene-bridged systems [(OC)₃M(μ -C₅H₄C₅H₄)M'(CO)₂] (M = Mo, W; M' = Fe, Ru) can be broken under electrocatalytic conditions to give a zwitterionic species in which the electron pair of the M–M' bond resides exclusively on the early metal center.^{220,221}

Use of the stannylated derivative Me₂Si(C₅H₄)₂-SnMe₂ allows the stepwise ligation of the two cyclopentadienyl rings. Hence, the compounds [Cl₂CpM(μ -C₅H₄SiMe₂C₅H₄)Rh(cod)] (M = Ti, Zr) have been prepared by reaction first with CpMCl₃ and then with [RhCl(cod)]₂.²²²

A carbonyl-bridged bis(cyclopentadienyl) ligand can be prepared by reaction of Li⁺C₅Me₄H⁻ with [(η ⁵-C₅H₄COOMe)WMe(CO)₃]. This metalloligand, either in its deprotonated form or as a silyl enol ether, reacts with a number of late metal precursors under mild conditions to give [(OC)₃MeW(μ -C₅H₄COC₅HMe₄)-ML_{*n*}] (ML_{*n*} = Fe(CO)₂, Ru(CO)₂, Co(CO)₂, Rh(CO)₂, Rh(nbd)). The X-ray crystal structures of the ML_{*n*} = Ru(CO)₂, Co(CO)₂, and Rh(nbd) complexes have been obtained. Only in the tungsten–ruthenium complex is there a short metal–metal contact (2.978 Å).²²³ In a similar manner, the pendant cyclopentadienyl ring of [Rh(C₅H₄CH₂C₅H₄)L₂] (L₂ = (CO)₂, (PⁱPr₃)(PhC≡CPh)) can be coordinated to a niobium or a molybdenum center by reaction with [CpNb(N^tBu)Cl₂] or [Mo(N^tBu)₂Cl₂], respectively.²²⁴ Reaction of [(η ⁵-C₅H₄-COC₅HMe₄)WMe(CO)₃] with an excess of iron pentacarbonyl in refluxing diglyme results in the reduction of the organic carbonyl group, giving [(OC)₃MeW(μ -C₅H₄COC₅HMe₄)Fe(CO)₂] in 13% yield.²²³

7. Other Dianionic-Bridged Compounds

The products of the reaction between the titanium dithiolate complexes [CpTi{S(CH₂)_{*n*}S}₂] (*n* = 2, 3) and rhodium(I) or copper(I) precursors are polymeric. Addition of a suitable ligand to complete the coordination sphere of the late metal (nbd in the case of rhodium, PMe₃ in the case of copper) leads to discrete complexes, [CpTi{ μ -S(CH₂)_{*n*}S- κ TiS, κ TiS, κ CuS, κ CuS}]-Cu(PMe₃)] (*n* = 2, 3) and [CpTi{ μ -S(CH₂)₃S- κ TiS, κ TiS, κ RhS, κ RhS}]-Rh(nbd)] (see Figure 44) of which have been crystallographically characterized. This latter complex decomposes in solution to give the titanium(III)–dirhodium(I) complex [CpTi{ μ -S(CH₂)₃S}]-

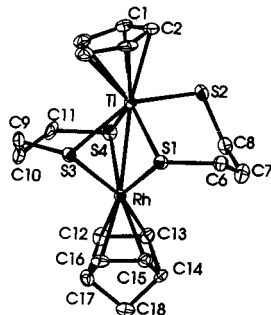


Figure 44. Crystal structure of [CpTi(μ -SCH₂CH₂CH₂S)-Rh(nbd)]. Reprinted from ref 225. Copyright 1994 American Chemical Society.

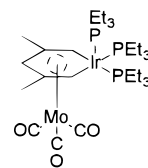


Figure 45. Coordination of “iridiabenzene”, [(Et₃P)₃-IrCHCMeCHCMeCH], to a Mo(CO)₃ fragment. Redrawn from ref 226.

{Rh(nbd)}₂], the crystal structure of which has also been determined.²²⁵

The aromatic metallacyclic compound [(Et₃P)₃-IrCHCMeCHCMeCH] can coordinate to a Mo(CO)₃ fragment in the same way as a benzene ring (see Figure 45). Protonation of the resulting bimetallic compound yields a μ -hydrido species in which the η ⁶-coordination is preserved but with a slight shortening of the Mo–Ir distance (2.854 Å).²²⁶

The [(dimethylamino)methyl]ferrocene [CpFe(C₅H₄-CH₂NMe₂)] can be readily *ortho*-lithiated, producing a potentially tridentate bridging ligand between iron and an early metal center.²²⁷ When this is reacted with [Cp₂MCl₂] (M = Ti, Zr), the resulting complexes [Cp₂M{(μ - η ¹_M, η ⁵_{Fe}-(Me₂NCH₂)C₅H₃)FeCp}₂] contain a bidentate bridging ligand with a pendant amino-methyl group.²²⁸ The monosubstituted product [Cp₂-ClTi{ μ - η ¹_{Ti}, η ⁵_{Fe}-(Me₂NCH₂)C₅H₃)FeCp] has also been prepared and crystallographically characterized.²²⁹ Using the titanium(III) precursor [Cp₂TiCl]₂ or the masked zirconium(IV) precursor [Cp₂Zr(1-camphenyl)Cl] leads to complexes containing the tridentate bridging ligand with chelation at the early metal center.²²⁸ use of [CpTiCl₃] gave the species [CpCl₂-Ti(μ -Me₂NCH₂C₅H₃- κ TiN, κ TiC, κ FeCp)FeCp], [CpTi{(μ -Me₂NCH₂C₅H₃- κ TiN, κ TiC, κ FeCp)FeCp}]{ μ - η ¹_{Ti}, η ⁵_{Fe}-(Me₂NCH₂)C₅H₃)FeCp}], [CpClTi{(μ -Me₂NCH₂C₅H₃)-FeCp}₂], and [CpTi{(μ -Me₂NCH₂C₅H₃)FeCp}₃], the crystal structures of the first two of which were determined.²²⁹

When the *ortho*-lithiated ferrocene is reacted with [VCl₃(thf)₃] or MCl₅ (M = Nb, Ta), the chlorine atoms are substituted to varying degrees. The widest range of substitution is observed for niobium, with mono-, di-, and trisubstituted products being isolated.^{230,231} A range of vanadium–iron compounds has been prepared, and the ⁵⁷Fe Mössbauer spectra have been recorded: in certain complexes, there appears to be a polarization within the ferrocene ligands leading to a contribution to the signal from iron(III) species.²³² Molybdenum and tungsten complexes of this ligand have also been prepared, from [MoO₂(acac)₂] and [WOCl₄], respectively, as well as a number of lanthanide and actinide complexes.^{233,234}

The template synthesis of the dicationic copper(II) Schiff base complex [Cu{HOC₆H₄CH=N(CH₂)₃N=CHC₆H₄OH}₂]²⁺ allows a route for the preparation of heterobimetallic lanthanide–copper complexes. The lanthanide(III) centers are thought to be bound by two salicylidene oxygens, three water molecules, and a chloride ion.²³⁵

Reaction of [Cu(H₂teta)]²⁺ with MCl₄ (M = Ti, Zr) leads to deprotonation of the polyamine ligand and the formation of binuclear complexes [Cl₂M(μ -HN-(CH₂)₂NH(CH₂)₂NH(CH₂)₂NH- κ MN^I, κ MN^{IV}, κ CuN^I,

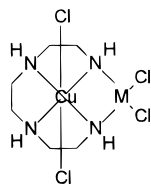


Figure 46. Proposed structure of $[\text{Cl}_2\text{M}\{\mu\text{-HN}(\text{CH}_2)_2\text{NH}-(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}\}\text{CuCl}_2]$ ($\text{M} = \text{Ti}, \text{Zr}$). Redrawn from ref 236.

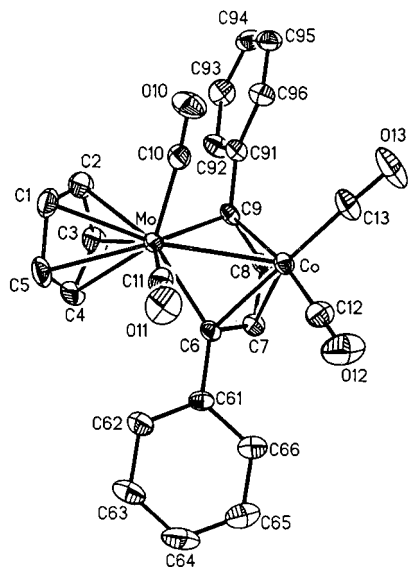


Figure 47. Crystal structure of $[(\text{OC})_2\text{CpMo}(\mu\text{-PhC}=\text{CHCH}=\text{CPh})\text{Co}(\text{CO})_2]$. Reprinted from ref 238. Copyright 1995 Elsevier Science Ltd.

$\kappa_{\text{Cu}}\text{N}^{\text{II}}, \kappa_{\text{Cu}}\text{N}^{\text{III}}, \kappa_{\text{Cu}}\text{N}^{\text{IV}}\text{CuCl}_2]$ (see Figure 46). The product complexes are nonelectrolytes in solution, and EPR measurements show g values indicative of octahedral copper(II).^{236,237}

The so-called flyover complexes have as a motif a metallocyclopentadiene ring, formed by the dimerization of coordinated alkynes, which is η^4 -bound to the second metal center. This has been formed by the reaction²³⁸ of phenylethyne with $[(\text{OC})_2(\text{Ph}_3\text{P})\text{CpMoCo}(\text{CO})_3(\text{PPh}_3)]$ to give $[(\text{OC})_2\text{CpMo}(\mu\text{-}\eta^2\text{Mo}, \eta^4\text{Co}\text{-PhC}=\text{CHCH}=\text{CPh})\text{Co}(\text{CO})_3]$ (see Figure 47) or by the reaction²³⁹ of $\text{Co}_2(\text{CO})_8$ or $\text{Fe}_2(\text{CO})_9$ with $[\text{MoCpCl}(\text{RC}=\text{CR}')_2]$ ($\text{R}, \text{R}' = \text{Me}, \text{Ph}$).

Floriani and co-workers have prepared the titanium–iron complex $[\text{Cp}_2\text{CITi}(\mu\text{-OC}=\text{CH}_2\text{-}\kappa_{\text{Ti}}\text{O}, \kappa_{\text{Fe}}\text{C})\text{FeCp}(\text{CO})(\text{PPh}_3)]$, from which the compounds $[\text{Cp}_2\text{-CITi}(\mu\text{-OCHPhCH}_2\text{CO-}\kappa_{\text{Ti}}\text{O}, \kappa_{\text{Fe}}\text{C})\text{FeCp}(\text{CO})(\text{PPh}_3)]$ and $[\text{Cp}_2\text{Ti}(\mu\text{-OCHPhCH}_2\text{CO-}\kappa_{\text{Ti}}\text{O}, \kappa_{\text{Ti}}\text{O}', \kappa_{\text{Fe}}\text{C})\text{FeCp}(\text{CO})(\text{PPh}_3)]^+$ (see Figure 48) can be prepared by reaction with benzaldehyde and subsequent removal of chloride, respectively. These compounds are important as models of the intermediates in the stereospecific transfer of acyl groups by the anion $[\text{CpFe}(\text{COCHR})(\text{CO})(\text{PPh}_3)]^-$.²⁴⁰

The complex $[\{\text{HC}(\text{SiMe}_2\text{NC}_6\text{H}_4\text{F})_3\}\text{Zr}(\mu\text{-OC}_6\text{H}_2\text{R}_2\text{-C}_{10}\text{H}_6\text{-}\kappa_{\text{Zr}}\text{O}, \kappa_{\text{Fe}}\text{C})\text{FeCp}(\text{CO})_2]$ ($\text{R} = \text{Me}, \text{OMe}$) has been prepared by the slow spontaneous decarbonylation of $[\{\text{HC}(\text{SiMe}_2\text{NC}_6\text{H}_4\text{F})_3\}\text{Zr}(\mu\text{-OC}_6\text{H}_2\text{R}_2\text{-C}_{10}\text{H}_6\text{CO-}\kappa_{\text{Zr}}\text{O}, \kappa_{\text{Zr}}\text{O}', \kappa_{\text{Fe}}\text{C})\text{FeCp}(\text{CO})_2]$ (see section V.K). The $\text{R} = \text{OMe}$ complex has been crystallographically characterized (see Figure 49).²⁴¹

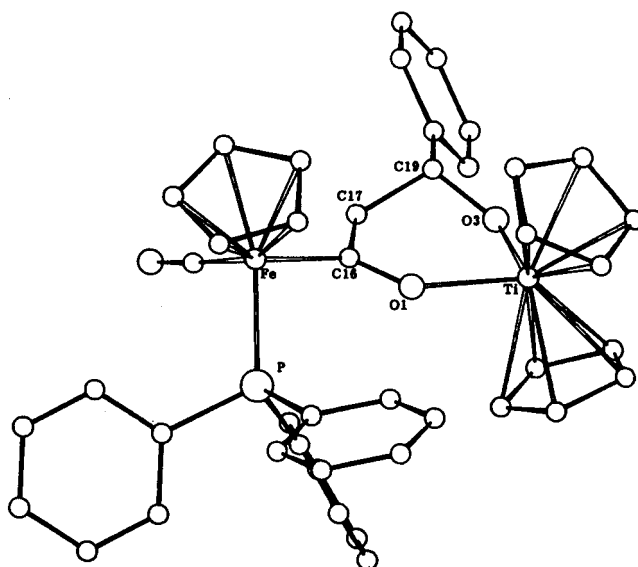


Figure 48. Crystal structure of $[\text{Cp}_2\text{Ti}(\mu\text{-OCHPhCH}_2\text{CO})\text{-FeCp}(\text{CO})(\text{PPh}_3)]^+$. Reprinted from ref 240. Copyright 1990 American Chemical Society.

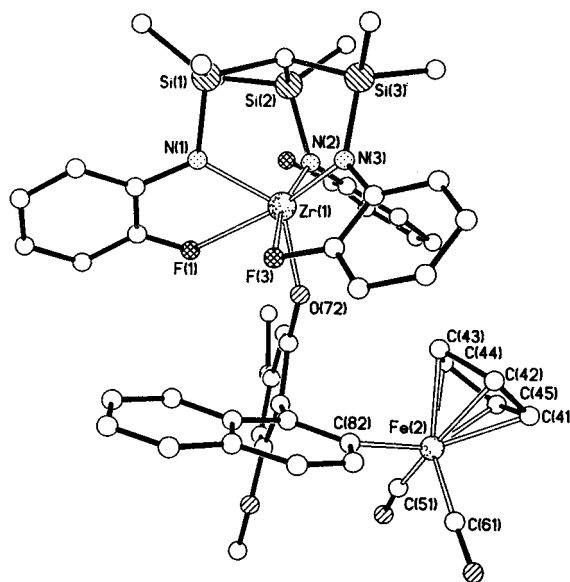


Figure 49. Crystal structure of $[\{\text{HC}(\text{SiMe}_2\text{NC}_6\text{H}_4\text{F})_3\}\text{Zr}(\mu\text{-OC}_6\text{H}_2(\text{OMe})_2\text{C}_{10}\text{H}_6)\text{FeCp}(\text{CO})_2]$. Reprinted from ref 241. Copyright 1998 American Chemical Society.

E. Compounds Containing Trianionic Bridging Ligands

1. Alkylidyne-Bridged Compounds

Bermúdez and Stone²⁴² have used the tungsten carbyne fragment $[\text{CpW}(\text{CR})(\text{CO})_2]$ to prepare alkylidyne-bridged tungsten–rhodium complexes by reaction with $[\text{Rh}(\text{PPh}_3)_2(\text{cod})]^+$. The tungsten–gold complexes $[(\text{CO})_2\text{LW}(\mu\text{-CMe})\text{Au}(\text{PPh}_3)]^+$ ($\text{L} = \text{Cp}, \text{Tp}$) have been similarly prepared.

Reaction of the molybdenum terminal alkylidyne complex $[\text{Cp}^*\text{Mo}(\text{CO})_2(\text{CC}_6\text{H}_3\text{Me}_2)]$ with $\text{Fe}_2(\text{CO})_9$ results in the formation of an alkylidyne-bridged species, $[(\text{OC})_2\text{Cp}^*\text{Mo}(\mu\text{-CC}_6\text{H}_3\text{Me}_2)\text{Fe}(\text{CO})_3]$. This reacts further with dppm to provide $[(\text{OC})\text{Cp}^*\text{Mo}(\mu\text{-CC}_6\text{H}_3\text{Me}_2)(\mu\text{-dppm})\text{Fe}(\text{CO})_2]$. Reaction of the starting molybdenum complex with a source of “ Cp^*Cu ” gives the

molybdenum–copper complex $[(OC)Cp^*Mo(\mu-CC_6H_3Me_2)(\mu-CO)CuCp^*]$.¹⁷⁰ Similarly, $[CpM(\equiv CTol)(CO)_2]$ ($M = Mo, W$) reacts with the cyclopalladated azaphenanthroline complexes $[Pd(\mu-Cl)(C_{13}H_8N-C,N)]_2$ to give $[(OC)_2CpM(\mu-CTol)PdCl(C_{13}H_8N-C,N)]$, the tungsten–palladium complex of which has been crystallographically characterized.¹⁹⁸

2. Other Trianionic-Bridged Compounds

Acetylene-substituted carbenes $[(OC)_5M\{=C(NMe_2)-C\equiv CR\}]$ ($M = Cr, W; R = H, SnBu_3$) can be attached to late metal fragments either by nucleophilic substitution of a halide ligand or by Heck coupling. Heterobimetallic complexes which have been prepared in this manner include $[(OC)_5M=C(NMe_2)C\equiv C-M'L_n]$, in which $M'L_n$ is $FeCp(CO)_2$, $Rh(CO)(PPh_3)$, $NiCp(PPh_3)$, or $Ni(\text{mesityl})(PMe_2Ph)_2$. Several of the tungsten complexes have been crystallographically characterized.²⁴³

The vanadium silylimido compounds $[V(NSiR_3)(OSiR_3)_3]$ ($R = Me, Et$) react with the labile group 9 precursors $[MF(CO)(PPh_3)_2]$ ($M = Rh, Ir$) to give the nitrido-bridged heterobimetallic complexes $[(R_3SiO)_3V=N-M(CO)(PPh_3)_2]$.²⁴⁴

The chiral substituted ferrocene $[CpFe(C_5H_4CHN-H^iPrCH_2C_5HMe_4)]$ can be prepared in 45% overall yield and 98% ee from a chloro-functionalized ferrocenyl ketone. The chiral metalloligand was readily bound to a titanium center through the cyclopentadienyl ring and the amide functionality.²⁴⁵

F. Compounds Containing Polyanionic Bridging Ligands

The unbridged zirconium–iron complex $[\{HC(SiMe_2NC_6H_4F)_3\}ZrFeCp(CO)_2]$ reacts with the δ -lactone $C_6H_2R_2COOC_{10}H_6$ ($R = Me, OMe$) with opening of the lactone ring and cleavage of the Zr–Fe bond to give $[\{HC(SiMe_2NC_6H_4F)_3\}Zr(\mu-OC_6H_2R_2C_{10}H_6CO-\kappa_{Zr}O, \kappa_{Zr}O, \kappa_{Fe}C)FeCp(CO)_2]$ (see Figure 50 and section

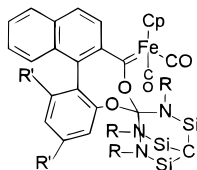


Figure 50. Proposed structure of $[\{HC(SiMe_2NC_6H_4F)_3\}Zr(\mu-OC_6H_2R_2C_{10}H_6CO)FeCp(CO)_2]$ ($R = Me, OMe$). Redrawn from ref 241.

V.K). This complex undergoes slow spontaneous decarbonylation with the iron center attaching itself to the naphthalene ring (see section III.D.7).²⁴¹

The iron(II)–vanadium(III) complex of an aminophenolato imido macrocycle has been prepared and crystallographically characterized (see Figure 51). Reaction of this complex with trimethyliodosobenzene leads to oxidation of the vanadium to the +4 state, but leaves the oxidation state of the iron center unchanged (see section V.D). The X-ray crystal structure of the product complex has also been determined.²⁴⁶

The lanthanum complex of the tripodal ligand prepared by condensation of tris(2-aminoethyl)amine

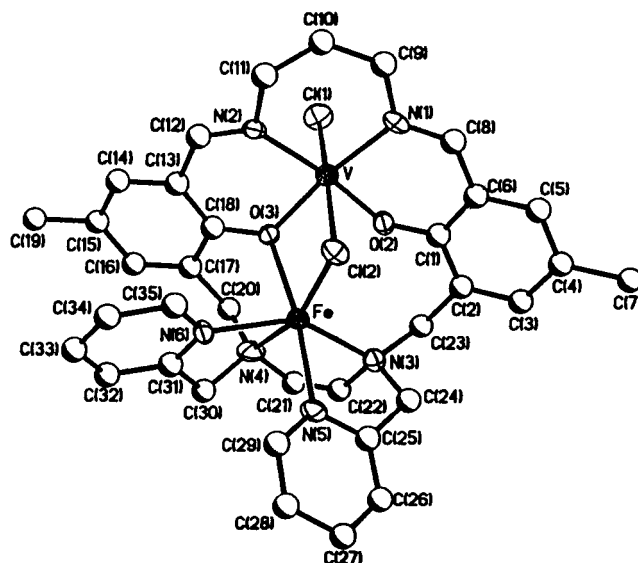


Figure 51. Crystal structure of $[Fe(\text{entnim})(\mu-Cl)VCl]^+$. Reprinted from ref 246. Copyright 1997 American Chemical Society.

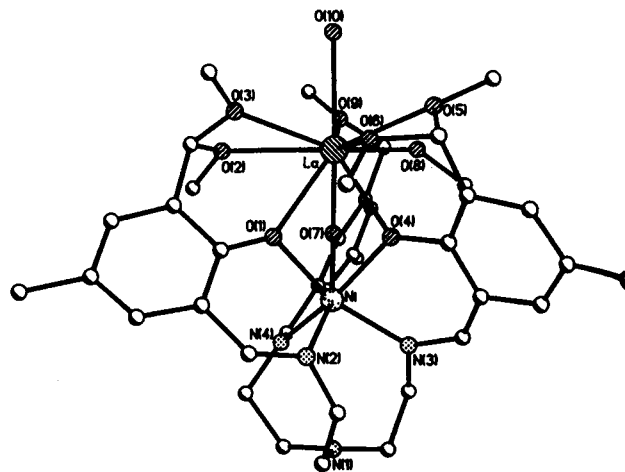


Figure 52. Crystal structure of $[(H_2O)La\{\mu-N[CH_2-CH_2N=CHC_6H_2Me(O)CH(OMe)_2]_3\}Ni]$. Reprinted from ref 247. Copyright 1997 Royal Society of Chemistry.

with 2,6-diformyl-4-methylphenol reacts with $Ni(ClO_4)_2$ to give a complex in which the two metal atoms are encapsulated within the potentially dodecadentate ligand: the X-ray crystal structure has been obtained (see Figure 52).²⁴⁷

The existence of gadolinium–iron heterobimetallic complexes of diethylenetriamine–pentaacetic acid bis(salicylamide) has been demonstrated in solution, but no solid-state characterization was carried out.²⁴⁸

G. Metallomacrocyclic Compounds

Titanocene and zirconocene dithiolate complexes $[Cp_2M\{S(CH_2)_nS\}MCp_2]$ ($M = Ti, Zr; n = 2, 3$) have the capacity to act as metallomacrocyclic ligands. Thus, copper and silver complexes of these metalloligands have been prepared:^{249–252} the late metals are bound in a pseudotetrahedral manner by the bridging sulfur atoms, as shown by X-ray crystal structures (e.g., Figure 53). Cyclic voltammetric studies of the titanium complexes showed a rare reversible $Ti(IV)/Ti(III)$ couple. Reduction could also be carried out

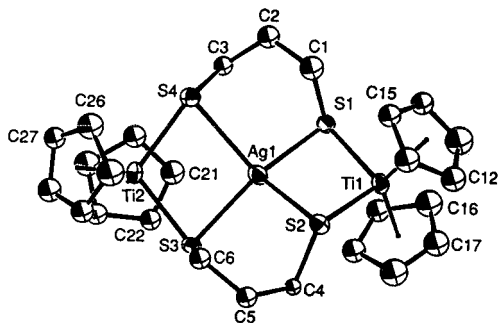


Figure 53. Crystal structure of $[\{\text{Cp}_2\text{Ti}(\mu\text{-SCH}_2\text{CH}_2\text{CH}_2\text{S})_2\text{-TiCp}_2\}\text{Ag}]$. Reprinted from ref 249. Copyright 1992 American Chemical Society.

chemically with Cp_2Co , and the EPR spectra of the neutral Ti(III)–M(I)–Ti(IV) complexes show a hyperfine coupling of the unpaired electron on titanium ($g = 1.9821, 1.9817$; $a_{\text{Ti}} = 10.5, 11.0$ G) with $^{63,65}\text{Cu}$ or $^{107,109}\text{Ag}$ ($a_{\text{Cu}} = 3.5$ G; $a_{\text{Ag}} = 5.0$ G).²⁴⁹ Reaction of certain titanium metallocycles with nickel or palladium leads to complete ligand transfer and the formation of nickel or palladium thiolate complexes.²⁵⁰ However, the zirconium–palladium metallocyclic complex $[\text{Pd}\{\text{Cp}_2\text{Zr}(\text{SCH}_2\text{CH}_2\text{S})\text{ZrCp}_2\}]$ has been prepared by the reaction of $[\text{Cp}_2\text{ZrH}_2]$ with $[\text{Pd}(\text{SCH}_2\text{CH}_2\text{S})(\text{PPh}_3)_2]$: it has a Zr–Pd distance of 2.866 Å.²⁵³

IV. Metal–Metal Interactions in Heterobimetallic Compounds

Each of the metal centers in a bimetallic complex might be expected to affect the properties of the other, at least if the distance between them is sufficiently short. This interaction between the two centers can arise in several ways.

There may be a direct metal–metal bond, involving the sharing of one or more pairs of electrons between the centers. Such a bond could either be “covalent” in nature, involving electrons which would otherwise be unpaired on their respective metal centers, or “dative”, involving the donation of an otherwise nonbonding pair of electrons from one center to the other.

The properties of a donor atom in a bridging ligand may be modified by simultaneous coordination to the other metal center. Hence, the analogy between group 4 and group 5 terminal phosphido complexes and organophosphine ligands may only be approximate at best.

The coordination sphere of the second metal center might also be expected to have a significant steric effect on the first.

For a given complex, three questions arise: is there a significant interaction between the metal centers, and if so, how large is it and what is its nature?

A. Evidence from Crystallography

Examination of the crystallographic data reveals a modal value for the metal–metal distance in early–late heterobimetallic complexes of around 2.9 Å. A second mode appears at around 3.4 Å, although this is of more questionable statistical significance. It is

tempting to regard metal–metal distances of less than 3 Å as indicative of metal–metal bonding; however, this is not necessarily the case. The combination of normal metal–ligand bond lengths and angles can lead to metal–metal distances in this range without any need to invoke a direct metal–metal interaction. But there must be a certain distance below which the energy levels of the metal centers would be significantly perturbed in a bimetallic complex vis-à-vis those of a mononuclear complex. The question arises as to whether it is possible to estimate this distance a priori for a generalized system.

In unbridged systems, we note that the metal–metal distances are among the shortest observed (2.5–2.6 Å). However, these unbridged metal–metal bonds must also be among the strongest, insofar as they exist in isolable and characterizable compounds. Marks and co-workers have measured the dissociation energies of the unbridged uranium–iron and uranium–ruthenium bonds in $[\text{Cp}_3\text{UMCp}(\text{CO})_2]$ (M = Fe, Ru) at 129(13) kJ mol^{−1} (M = Fe) and 169(17) kJ mol^{−1} (M = Ru).²⁵⁴ It is difficult to draw conclusions as to the existence or otherwise of longer and weaker bonding interactions which must be bridged to be observable.

The minimum interaction which could occur between the two metal centers would be one based solely on electron correlation, not involving any orbital hybridization. In effect, this would be a type of van der Waals contact between the two metal centers. The van der Waals radii of metallic elements are poorly defined,²⁵⁵ but an estimation of their magnitude can be drawn from the $d^{10}\text{--}d^{10}$ interaction in compounds of silver(I) and gold(I),^{256,257} also based solely on electron correlation, which lead to metal–metal distances of 3.0–3.2 Å. It is credible, therefore, that the mode observed in the distribution of metal–metal distances at around 3.4 Å is due to a correlation interaction of this nature.

This would imply that all metal–metal contacts shorter than this lead to a perturbation of the orbital energies of the metal centers. However, it is not possible to predict a priori if this perturbation leads to a reduction in energy (bonding) or to an increase. Even if the metal–metal interaction is weakly antibonding, the complex could still be stabilized by the increased metal–ligand bond energy.

B. Evidence from Spectroscopy and Chemical Reactivity

As the X-ray crystal structure gives little information as to the nature of the metal–metal interaction in a given complex, it is necessary to search for other evidence. Although spectroscopy could, in principle, provide a valuable insight into the electronic structure at the frontier orbital level, few studies have been carried out.

The EPR spectra of the cyclooctatetraene-bridged complexes $[(\text{C}_5\text{R}_5)\text{Cr}(\mu\text{-}\eta^5\text{C}_8\text{R}_2\text{Fe}^3\text{-cot})\text{Fe}(\text{CO})_2\text{L}]$ (R = H, Me; L = CO, PMe_3 , PPh_3 , $\text{P}(\text{OEt})_3$, PF_3) clearly show hyperfine splitting by phosphorus (except for L = CO), with $a_{\text{iso}}(^{31}\text{P})$ varying from 13.3 G (R = H; L =

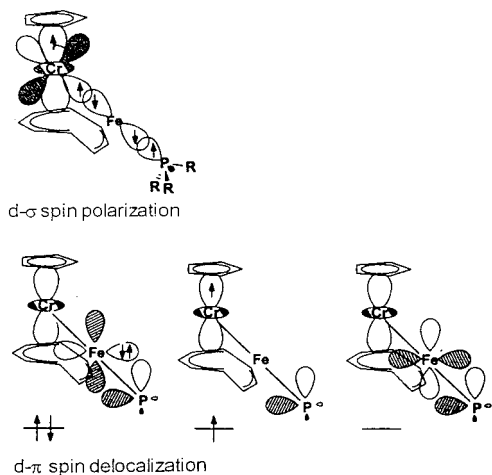


Figure 54. Proposed spin delocalization mechanism in $[(C_5R_5)Cr(\mu\text{-cot})Fe(CO)_2(PR_3)]$. Redrawn from ref 61.

PMe_3) to 34.2 G ($R = Me$; $L = PF_3$). The solid solution spectra show broad lines due to unresolved coupling to the hydrogens of the cyclooctatetraene, but A_{\perp} and A_{\parallel} are roughly the same. The authors propose a spin delocalization mechanism involving both σ - and π -interactions between the two metal centers (see Figure 54). Spin transfer through the bridging ligand was formally excluded.⁶¹

The ^{59}Fe Mössbauer spectra of $[(OC)_5W(\mu\text{-PPh}_2)FeCp(CO)_2]$ ($r(W\text{-}Fe) = 4.211 \text{ \AA}$) and $[(OC)_4W(\mu\text{-PPh}_2)(\mu\text{-CO})Fe(CO)]$ ($r(W\text{-}Fe) = 2.851 \text{ \AA}$) show isomer shifts of 0.0797 and 0.2914 $mm\ s^{-1}$, respectively. The increase in δ with the reduction in tungsten–iron distance was interpreted as the formal replacement of a carbonyl ligand on iron with a dative bond to the tungsten center: as the tungsten center is not significantly π -acidic, this would be expected to increase the d shielding orbital density on iron, and hence the isomer shift.⁸⁹ However, the available ^{59}Fe Mössbauer data for heterobimetallic complexes are as yet too few to draw firm conclusions.

The bulk of the data concerning metal–metal interactions comes from studies of the chemical reactivity of heterobimetallic complexes. Examples of altered reactivity due to direct metal–metal bonding or due to an interaction communicated by the bridging ligands can be found in sections V and VI below. However, it is not always easy to distinguish between the two.

There is no ambiguity in the case of the unbridged titanium–cobalt complexes studied by Selent and co-workers. In these, the titanium center causes a labilization of the ligand bound in the *trans*-position on the cobalt center.^{19,22} Similarly, in the indenyl-bridged chromium–rhodium complexes studied by Cecon and co-workers, the rate of ligand substitution at rhodium is increased 50-fold by the coordination of the $Cr(CO)_3$ fragment to the *trans*-face of the indenyl ligand. In this case, the metal centers are more than 5 \AA apart, and the effect of the second metal center could only be transmitted through the bridging indenyl ligand.¹⁵⁶

Clear examples of the steric effect of the second metal center are harder to find, but it is notable that the *cis*- $[(OC)_3Cr(\mu\text{-indenyl})RhL_2]$ complexes are inac-

tive as alkyne cyclotrimerization catalysts, whereas the *trans*-isomers have a very high activity.²⁷³

C. Theoretical Models

A number of groups have addressed these questions with the help of EHMO calculations. For bridged systems, thiolato²⁵⁸ and phosphido^{82,259} complexes of which have been the most studied, the calculated overlap populations are very low (<0.1). This would imply that the complexes are stabilized almost entirely by the additional metal–ligand interactions of the bridging ligands. Ferguson et al. have studied a system where the overlap population is much higher (0.649), $[Cp^*Zr(\mu\text{-OCH}_2PPh_2)_2RhMe_2]$.¹⁴ It is worth noting that this complex has an exceptionally short metal–metal distance (2.44 \AA). The overlap populations in orbitals bonding in a σ - or π -manner are almost the same, and the authors have proposed the existence of a zirconium–rhodium double bond. The overlap population calculated for the carbonyl-bridged species $[(OC)CpMo(\mu\text{-CO})_2Rh(PPh_3)_2]$ is intermediate at 0.185, despite the short Mo–Rh distance (2.59 \AA). Although it appears that there is some dative bonding from rhodium to molybdenum, the majority of the labile electron density on the rhodium center appears to be donated to the bridging carbonyl ligands.¹⁴

The situation is slightly different for unbridged complexes, in which there are undeniably metal–metal interactions. The zirconium–ruthenium complex $[Cp_2^tBuO)ZrRuCp(CO)_2]$ is calculated to have an overlap population of 0.336, despite a metal–metal distance of 2.91 \AA , similar to those of thiolato- or phosphido-bridged compounds. Selent et al. found overlap populations of around 0.2 in unbridged titanium–cobalt complexes.¹⁹

The most complete calculational study of unbridged heterobimetallic complexes is that recently published by Gade and co-workers.²⁶⁰ The model complexes $[(H_2N)_3TiCo(CO)_3L]$ ($L = CO, PH_3$) were investigated by DFT methods, using both gradient-corrected and hybrid basis sets. The residual atomic charge on the titanium center is highly positive when calculated using either the natural population analysis model or Bader's atoms in molecules model. The two models disagree as to the charge on the cobalt center, but both indicate a significant negative charge for the $Co(CO)_3L$ fragment. The bond order between the titanium and the cobalt is less than 0.5 when calculated either by Wiberg's model or by that of Bader. A local maximum in the electron localization function (ELF) is observed between the two metal centers, but its magnitude is only 0.46 (c.f. 0.8 for most covalent bonds). Hence, the bond is obviously highly polar, and the contribution of electrostatic interactions is shown by the increase in bond order (+0.1) on changing the ligand *trans* to titanium from CO to PH_3 . However, the authors still consider the interaction to be essentially covalent, and more so than for the donor–acceptor bonds in cobalt–group 13 heterobimetallics. This study also indicated that the stability of group 4–cobalt heterobimetallic complexes containing tripodal ligands is enhanced by the inability of the titanium to attain a trigonal-planar

coordination after the dissociation of the metal–metal bond.

D. Conclusion

It is reasonable to accept that early–late heterobimetallic compounds with particularly short intermetallic distances (<2.7 Å) or with low formal valence electron counts (32 electrons for a bimetallic system) contain direct metal–metal bonds, and that these bonds are essentially covalent in nature, highly polarized in early–late complexes, with a small but nonnegligible orbital overlap. This is not to deny the possibility of metal–metal bonding at longer interatomic separations or in 34-electron complexes: unbridged heterobimetallic complexes can have bond lengths up to 2.95 Å.²⁷ However, other descriptions of the metal–metal interaction, such as a polarization of the bridging ligands, may well be equally valid in these cases. Finally, despite the unquestioned crystallographic interest of metal–metal bonding, perhaps the more pertinent question is “does this affect the chemistry of the compound?”

V. Stoichiometric Reactivity

A. Ligand Substitution

Reports of simple ligand substitution, usually of a carbonyl by a more or less basic phosphine, are relatively common, and space does not permit us to list them all. However, certain of these reactions, discussed below, do have a less usual character that may be linked to the bimetallic nature of the complex.

Ceccon and co-workers have shown that substitution of the two carbonyl ligands on rhodium in the complex $[(OC)_3Cr(\mu\text{-indenyl})Rh(CO)_2]$ by cyclooctadiene is 2000 times faster than in the monometallic complex $[Rh(\eta^5\text{-indenyl})(CO)_2]$.¹⁵⁶ This rate enhancement does not seem to be a purely inductive effect: substitution of the six-membered ring by a nitro group leads only to a 5-fold enhancement in rate, although $-NO_2$ and $-Cr(CO)_3$ have similar Hammett σ -values. It appears that the simultaneous coordination of two 12-electron metal fragments to the 10π aromatic ligand leads to a situation where both metal centers have a certain coordinative unsaturation: there is NMR evidence to support this proposition.¹⁵⁷

The *trans*-effect of the directly bonded metal center can be seen in the complex $[(t\text{-BuO})_3TiCo(CO)_4]$, in which the carbonyl ligand *trans* to titanium is preferentially substituted by PPh_3 . It is not apparent from the published results whether this effect is caused by a weakening of the *trans* cobalt–carbon bond or by a strengthening of the *cis* bonds.^{19,22}

The cyclopentadienyl ligand bound to the palladium center of $[Cp_2Ta(\mu\text{-CH}_2)_2PdCp]$ is selectively substituted on reaction with a tertiary phosphine or phosphite ligand. When the reaction is carried out in dichloromethane solution, the final isolated product is $[Cp_2Ta(\mu\text{-CH}_2)_2PdCl(PR_3)]$. Use of the diphosphine ligand dmpe in acetonitrile solution allows the isolation of $[Cp_2Ta(\mu\text{-CH}_2)_2Pd(dmpe)]^+Cp^-$, the X-ray crystal structure of which has been determined.¹⁹⁴

It is also possible in certain cases to substitute a bridging ligand while the bimetallic framework is retained. The η^2 -phenyl ligand in $[(OC)CpMo(\mu\text{-CO})(\mu\text{-TolCC}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-}\kappa_{Mo}Tol(\eta^2),\kappa_{Mo}C,\kappa_{Pd}C,\kappa_{Pd}N)\text{-PdI}]$, as well as the terminal carbonyl ligand, is substituted at room temperature by *tert*-butyl isocyanide.²⁰⁰ Similarly, a bridging carbonyl and a terminal carbonyl are substituted on reaction of $[MoFe_2(\mu_3\text{-CTol})(\mu\text{-CO})Cp(CO)_8]$ with elemental selenium, to give $[MoFe_2(\mu\text{-CTol})(\mu_3\text{-Se})Cp(CO)_7]$.¹⁶⁹

When the tungsten–platinum complex $[(OC)_2CpW(\mu\text{-PCy}_2)Pt(CO)(PCy_2H)]$ is reacted with nitric oxide, the substitution of CO by NO occurs exclusively on the tungsten center.⁹⁸ When carbon monoxide is the incoming ligand, in the case of the substitution of cyclooctadiene in $[(OC)_3Cr(\mu\text{-indenyl})Ir(cod)]$ by CO (see also section V.F), the product formation is dependent on CO concentration. With bubbling of CO at low temperature, $[(OC)_3Cr(\mu\text{-}\eta^6_{Cr},\eta^1_{Ir}\text{-indenyl})Ir(cod)(CO)_2]$ is first formed: above 0 °C, complete substitution of the diolefin occurs, giving $[(OC)_3Cr(\mu\text{-}\eta^6_{Cr},\eta^1_{Ir}\text{-indenyl})Ir(CO)_4]$. If the reaction is performed using an atmosphere of CO above the solution, the sparingly soluble dimeric species $[(OC)_3Cr(\mu\text{-}\eta^6_{Cr},\eta^1_{Ir}\text{-indenyl})Ir(CO)_3]_2$ is the kinetic product.¹⁵⁸

B. Oxidative Addition

1. Protonation

The reaction of acids with heterobimetallic complexes has not been extensively studied, and in several cases leads to the destruction of the bimetallic framework. However, protonation of the molybdenum–iridabenzene complex $[(OC)_3Mo(\mu\text{-}\eta^6\text{-CHCMeCHCMeCHIr})(PEt_3)_2L]$ ($L = PMe_3, PEt_3, CO$) leads to a hydride-bridged species in which the Mo–Ir distance is 0.1 Å shorter than that in the parent complex.²²⁶

The bridging carbon dioxide ligand in $[Cp_2ClZr(\mu\text{-OCO-}\kappa_{Zr}O,\kappa_{Zr}O,\kappa_{Ru}C)RuCp(CO)_2]$ has a specific reactivity toward protic acids: the overall reaction yields $[(Cp_2ClZr)_2O]$ and $[CpRu(CO)_3]^+$.¹⁶⁶ Similarly, the acetyl bridge in $[Cp^*Zr(\mu\text{-OCH}_2PPh_2)(\mu\text{-OCMe-}\kappa_{Zr}O,\kappa_{Rh}C)(\mu\text{-Cl})Rh(CO)]$ reacts with HCl to give acetaldehyde (61% isolated yield) and $[Cp^*Zr(\mu\text{-OCH}_2PPh_2)(\mu\text{-Cl})_2Rh(CO)]$.¹⁴

Reaction of $[(OC)_2CpW(\mu\text{-PCy}_2)Pt(CO)(PCy_2H)]$ with HBF_4 leads to two products. For the most part, the hydride ligand is bridging the two metal centers, giving $[(OC)_2CpW(\mu\text{-PCy}_2)(\mu\text{-H})Pt(CO)(PCy_2H)]^+$, but the tungsten hydride species $[(OC)_2HCpW(\mu\text{-PCy}_2)Pt(CO)(PCy_2H)]^+$ has also been isolated and crystallographically characterized.⁹⁸

2. Reaction with Iodomethane

The nitrido-bridged heterobimetallic complex $[(Me_3SiO)_3V(\mu\text{-N})Ir(CO)(PPh_3)_2]$ reacts with iodomethane in a manner similar to that of Vaska's compound, with the methyl and iodo ligands bonding to the iridium center, which is formally oxidized to the +3 oxidation state.²⁴⁴ A similar reaction with $[Cp_2Ta(\mu\text{-CH}_2)_2Ir(CO)_2]$ results in the methylbis(carbonyl)iodo species: kinetic studies show that the oxidative

addition to the bimetallic complex is 60 times slower than that to $[\text{IrMe}(\text{CO})(\text{PPh}_3)_2]$.²⁶¹

The anionic compound $[(\text{OC})_2\text{CpW}(\mu\text{-Ph}_2\text{PC}_5\text{H}_4\text{-}\kappa\text{WP},\kappa\text{FeCp})\text{FeMe}(\text{CO})_2]^-$ reacts with iodomethane to form the neutral tungsten(II)–iron(II) species $[(\text{OC})_2\text{MeCpW}(\mu\text{-Ph}_2\text{PC}_5\text{H}_4\kappa\text{WP},\kappa\text{FeCp})\text{FeMe}(\text{CO})_2]$: in this case, the iodide ion does not bind to the metal center.¹¹³ Conversely, the reaction of iodomethane with $[(\text{thf})_3\text{I}_2\text{LaRuCp}(\text{CO})_2]$ leads to the cleavage of the lanthanum–ruthenium bond and to the formation of $[\text{LaI}_3(\text{thf})_3]$ and $[\text{CpRuMe}(\text{CO})_2]$: this can be seen as an indication of the polarity of the early–late metal–metal bond.²⁵

3. Reaction with Dihydrogen

The oxidative addition of H_2 to $[\text{Cp}_2\text{Ta}(\mu\text{-CH}_2)_2\text{Ir}(\text{CO})_2]$ has been extensively studied by Bergman et al. Reaction of this system with D_2 results in the incorporation of deuterium in the methylene bridges.²⁶² The closely related reaction with triorganosilanes has also been studied.^{261,263}

No oxidative addition product could be observed from the reaction of the related tantalum–platinum complex $[\text{Cp}_2\text{Ta}(\mu\text{-CH}_2)_2\text{PtH}(\text{PMe}_3)]$ with H_2 , although deuterium incorporation into the methylene bridges and at the hydride position was observed on reaction with D_2 .¹⁹⁷

The strained three-membered ring in $[\text{Cp}_2\text{Zr}(\mu\text{-N}^t\text{Bu})\text{IrCp}^*]$ is reactive toward H_2 , giving (reversibly) $[\text{Cp}_2\text{HZr}(\mu\text{-N}^t\text{Bu})(\mu\text{-H})\text{IrCp}^*]$. The fluxionality between bridging and terminal positions was shown by labeling studies.¹⁸⁰

In common with its reaction with iodomethane, $[(\text{Me}_3\text{SiO})_3\text{V}(\mu\text{-N})\text{Ir}(\text{CO})(\text{PPh}_3)_2]$ reacts with dihydrogen to give oxidative addition at the iridium center.²⁴⁴ Similarly, reaction of H_2 with the zirconium–rhodium complex $[\text{Cp}^*\text{Zr}(\mu\text{-OCH}_2\text{PPh}_2)_2\text{Rh}(\text{PPh}_3)]$ occurs only on the rhodium center, giving the expected dihydride.¹⁴

C. Insertion Reactions

The bimetallic methyl complex $[(\text{OC})_5\text{WFeMe}(\text{CO})_4]$ undergoes migratory insertion of the carbonyl into the iron–carbon bond on reaction with PPh_3 . The reaction is approximately 40 times faster than that of the monometallic species $[\text{FeMe}(\text{CO})_4]^-$. It is not clear if this enhancement is due to a Lewis acid–base interaction between the tungsten center and the acyl oxygen or to a diminution of the electron density at the iron center, although the authors propose the former explanation. The methyl complex also reacts with carbon disulfide, forming a dithioacetate-bridged species.³²

The complex $[\text{Cp}_2\text{Zr}(\mu\text{-N}^t\text{Bu})\text{IrCp}^*]$ reacts readily with a number of weak protic acids, e.g., ToINH_2 , $^t\text{BuOH}$, and CH_3COCH_3 . The zirconium–iridium bond is lost during this reaction, and the isolated products have a hydride bridge with the remaining anionic fragment bound to the zirconium center (see Figure 55). It is not immediately apparent why the hydride is the preferred bridging ligand, leaving the bimetallic system with only 32 electrons: this is possibly due to the steric hindrance of the C_5Me_5^- ligand, and it cannot be ruled out that the isolated

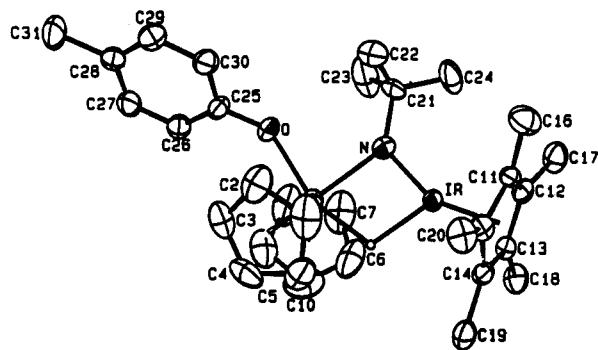


Figure 55. Crystal structure of $[(\text{TolO})\text{Cp}_2\text{Zr}(\mu\text{-H})(\mu\text{-N}^t\text{Bu})\text{IrCp}^*]$. Reprinted from ref 180. Copyright 1994 American Chemical Society.

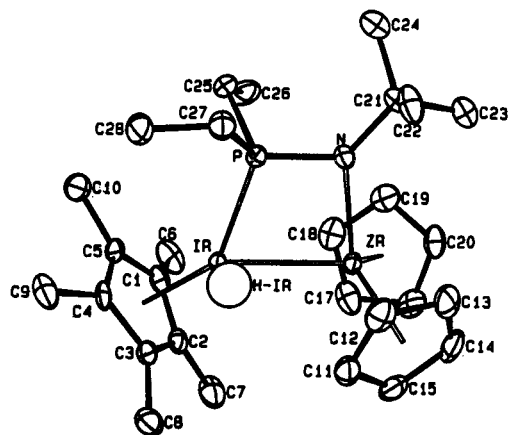


Figure 56. Crystal structure of $[\text{Cp}_2\text{Zr}(\mu\text{-N}^t\text{Bu})\text{IrCp}^*]$. Reprinted from ref 180. Copyright 1994 American Chemical Society.

compounds are the kinetic rather than the thermodynamic products. Reaction of the complex with dihydrogen or PhMeSiH_2 leads to similar products, indicating that the first step of the reaction may well be an oxidative addition at the iridium center. Addition of H_2S leads to the sulfido-bridged complex $[\text{Cp}_2\text{Zr}(\mu\text{-S})(\mu\text{-N}^t\text{Bu})\text{IrCp}^*]$, with elimination of H_2 . Addition of secondary phosphines gives insertion of the PR_2 group into the iridium–nitrogen bond, yielding $[\text{Cp}_2\text{Zr}(\mu\text{-N}^t\text{Bu})\text{PR}_2\text{-}\kappa\text{Zr},\text{N},\kappa\text{Ir},\text{P}]\text{IrHCp}^*$ (see Figure 56). The difference in reactivity may be explained by the softness of the phosphorus center and its low affinity for zirconium.^{179,180}

Allene and heteroallenes insert into the zirconium–iridium bond in a broadly similar manner. Hence, reaction with allene gives $[\text{Cp}_2\text{Zr}(\mu\text{-N}^t\text{Bu})(\mu\text{-}\eta^1\text{Zr},\eta^3\text{Ir-C}_3\text{H}_4)\text{IrCp}^*]$, and reaction with CO_2 gives $[\text{Cp}_2\text{Zr}(\mu\text{-N}^t\text{Bu})(\mu\text{-OCO-}\kappa\text{Zr},\text{O},\kappa\text{Ir},\text{O})\text{IrCp}^*]$. Reaction with methyl isocyanate leads to a rearrangement to give $[\text{Cp}_2\text{Zr}(\mu\text{-NMe})(\mu\text{-N}^t\text{BuCO-}\kappa\text{Zr},\text{N},\kappa\text{Ir},\text{C})\text{IrCp}^*]$ (see Figure 57).⁸ Finally, the complex also reacts with sulfur-containing organic molecules, e.g., CS_2 , COS , Me_3PS , and substituted thiiranes (alkene sulfides), to give the sulfido-bridged complex mentioned above. A similar reaction with oxygen donors, e.g., pyridine *N*-oxide, N_2O , and styrene oxide, forms the analogous oxo-bridged species.¹⁷⁸

The migratory insertion of carbon monoxide into a metal–carbon bond has been observed for carbon-based bridging ligands. Hence, reaction of $[\text{Cp}_2\text{CITi-}$

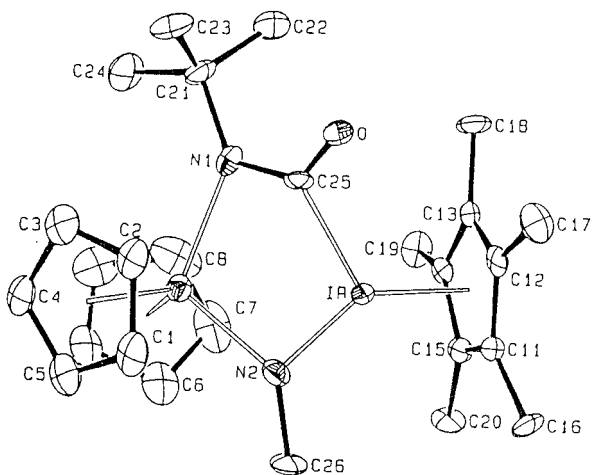


Figure 57. Crystal structure of $[\text{Cp}_2\text{Zr}(\mu\text{-NMe})(\mu\text{-N}^t\text{BuCO})\text{IrCp}^*]$. Reprinted from ref 8. Copyright 1995 American Chemical Society.

$(\mu\text{-CH}_2)\text{PtMe}(\text{PETe}_3)_2$ with CO gives a μ -ketene complex,¹⁹⁰ whereas reaction of CO with $[\text{Cp}_2\text{ClZr}(\mu\text{-CH=CH})\text{RuCp}(\text{PMe}_3)_2]$ affords a μ -propenyl bridging ligand.²¹⁰ Addition of PPh_3 to the molybdenum–iron complex $[(\text{OC})_3\text{CpMo}(\mu\text{-C}_3\text{H}_6)\text{FeCp}(\text{CO})_2]$ induces the migratory insertion of carbon monoxide into the propanediyl bridge. This reaction shows complete selectivity for the molybdenum center, and only $[(\text{OC})_2(\text{Ph}_3\text{P})\text{CpMo}(\mu\text{-COC}_3\text{H}_6)\text{FeCp}(\text{CO})_2]$ was isolated. In contrast, the tungsten–iron analogue shows the inverse behavior, giving $[(\text{OC})_3\text{CpW}(\mu\text{-C}_3\text{H}_6\text{CO})\text{FeCp}(\text{CO})(\text{PPh}_3)]$. The authors have rationalized this difference in reactivity by reference to monometallic model compounds.²⁰⁷

Even unbridged metal–metal bonds have been shown to react with appropriate substrates while the bimetallic nature of the products is retained. Thus, $[\{\text{MeSi}(\text{SiMe}_2\text{NTol})_3\}\text{MM}'\text{Cp}(\text{CO})_2]$ ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$; $\text{M}' = \text{Fe}, \text{Ru}$) reacts with methyl isocyanide to give a $\text{M}(\mu\text{-C=NMe})\text{M}'$ framework: this is analogous to the well-known α -addition reaction of an electrophile and a nucleophile to an isocyanide carbon.¹⁶ The reaction of isocyanides with $[\text{Cp}_2\text{ClZr}(\mu\text{-CH=CH})\text{RuCp}(\text{PMe}_3)_2]$ is similar to that of carbon monoxide, giving $[\text{Cp}_2\text{ClZr}(\mu\text{-}^t\text{BuN=C-CH=CH-}\kappa_{\text{Zr}}\text{C=N}, \kappa_{\text{Ru}}\text{C})\text{RuCp}(\text{PMe}_3)_2]$ (see Figure 42).²¹³

Heteroallenes insert into the early–late metal–metal bond (see above), with the central carbon atom being bound to the late metal center. Hence, CO_2 reacts with $[\text{Cp}_2\text{ClZrMCp}(\text{CO})_2]$ ($\text{M} = \text{Fe}, \text{Ru}$) to give $[\text{Cp}_2\text{ClZr}(\mu\text{-O}_2\text{C-}\kappa_{\text{Zr}}\text{O}, \kappa_{\text{Zr}}\text{O}, \kappa_{\text{M}}\text{O})\text{MCp}(\text{CO})_2]$.²⁶⁴ A number of heteroallenes have been shown to react with $[\{\text{HC}(\text{SiMe}_2\text{NAr})_3\}\text{ZrMCp}(\text{CO})_2]$ ($\text{M} = \text{Fe}, \text{Ru}$) in a completely analogous manner.²⁶⁵ Both groups postulate a mechanism in which the zirconium center acts as a Lewis acid, promoting the attack of the second metal center on the central carbon atom.

The complex $[\text{CpW}(\mu\text{-CO})_3\text{NiCp}^*]$ can be considered to contain a tungsten–nickel double bond, and accordingly behaves as a coordinatively unsaturated species. Its rapid reaction with sulfur dioxide affords a $\mu\text{-SO}_2$ complex which still contains a tungsten–nickel bond (2.652 Å).⁶⁵ The insertion of phenylacetylene into a bridging tungsten–carbonyl bond in

$[(\text{OC})\text{CpW}(\mu\text{-CO})_2\text{NiCp}^*(\text{CO})]$ has been reported, giving the nickelacyclobutenone flyover complex $[(\text{OC})_2\text{-CpW}\{\mu\text{-HC=CPhC(=O)-}\kappa_{\text{W}}\text{HC=CPh}, \kappa_{\text{Ni}}\text{C}, \kappa_{\text{Ni}}\text{C}'\}\text{-NiCp}^*]$. This insertion is reversible insofar as heating the complex leads to decarbonylation and the formation of the η^2 -alkyne-bridged species $[(\text{OC})\text{CpW}(\mu\text{-CO})(\mu\text{-PhC}\equiv\text{CH})\text{NiCp}^*]$.²⁶⁶

Finally, it is convenient to mention here the alkyne coupling reaction which occurs on $[(\text{OC})_2(\text{Ph}_3\text{P})\text{CpMoCo}(\text{CO})_3(\text{PPh}_3)]$ to give the flyover complex $[(\text{OC})_2\text{CpMo}(\mu\text{-}\eta^1\text{Mo}, \eta^1\text{Mo}, \eta^4\text{Co-PhC=CH-CH=CPh})\text{Co}(\text{CO})_2]$,²³⁸ and the insertion of benzaldehyde into the bridge of $[\text{Cp}_2\text{Ti}\{\mu\text{-OC(=CH}_2)\}\text{FeCp}(\text{CO})(\text{PPh}_3)]$ (see section III.D.7).²⁴⁰

Diazomethane reacts with $[\text{CpM}(\mu\text{-CO})_3\text{NiCp}^*]$ ($\text{M} = \text{Mo}, \text{W}$) to give the methylene-bridged compound $[(\text{OC})_2\text{CpM}(\mu\text{-CH}_2)(\mu\text{-CO})\text{NiCp}^*]$ in what could be described as an addition reaction on the 32-electron starting compound. 2-Butyne can insert into the Ni– CH_2 bond of the tungsten–nickel product, giving $[(\text{OC})\text{CpW}(\mu\text{-CH}_2\text{CMeCMe})(\mu\text{-CO})\text{NiCp}^*]$.²⁰²

D. Redox Reactions and Electrochemistry

Several groups have attempted to probe the interaction between two metal centers in heterobimetallic compounds by studying their redox processes. These reactions, either chemical or electrochemical, can be easily compared to those of monometallic model systems. A departure from the behavior predicted by a superposition of the properties of the two independent centers is strong evidence for a metal–metal interaction, either direct or through the intermediacy of the bridging ligands.

The titanium–iron metalloalkyne complex $[(\text{C}_5\text{H}_4\text{-SiMe}_3)_2\text{Ti}\{\mu\text{-C}\equiv\text{CC}_5\text{H}_4\}\text{FeCp}_2]$ shows a Ti(IV)/Ti(III) couple close to that seen for other bis(alkynyl)-titanocenes: $E_{1/2} = -0.74\text{ V}$;²⁶⁷ c.f. $E_{1/2} = -0.63\text{ V}$ for $[(\text{C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\text{C}\equiv\text{CSiMe}_3)_2]$. However, when a nickel(0) center is bound to form a pincer complex, the reduction potential of titanium passes to -2.37 V . It appears that the nickel center donates a significant electron density to the titanium, presumably through the α -carbons of the alkynes, although it cannot be ruled out that the effect is due to the greater rigidity of the complex, which would hinder the distortion of the coordination sphere required on passing from a $d^0\text{ Ti}^{\text{IV}}$ to a $d^1\text{ Ti}^{\text{III}}$ center.²⁰⁴

The opposite behavior is observed in metallo-macrocylic complexes $[(\text{Cp}_2\text{Ti}\{\mu\text{-S}(\text{CH}_2)_n\}_2\text{TiCp}_2\text{M}]^+$ ($\text{M} = \text{Cu}, n = 2$; $\text{M} = \text{Ag}, n = 3$) in which the presence of the coinage metal stabilizes the titanium(III) species. The reversible Ti(IV)/Ti(III) couples are observed at -0.77 V ($\text{M} = \text{Cu}$) and -1.10 V ($\text{M} = \text{Ag}$), whereas the metallomacrocylic ligands alone display only irreversible reduction processes. The titanium(III) complexes are sufficiently stable to be obtained by Cp_2Co reduction and to be characterized by ESR (see section III.G).²⁴⁹

The nickel(0) complex $[\text{Cp}_2\text{Ti}(\text{SCH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2\text{-Ni}]$, which is highly sensitive to oxygen and moisture, shows a nickel-based electrochemistry with reversible oxidation occurring at -0.51 and -0.06 V in two successive one-electron processes. However, the nickel(II) species is not sufficiently stable to be isolated.¹⁴²

The electrochemistry of three molybdenum–iron complexes with fulvalene-type bridges has been examined and compared to that of analogous monometallic complexes. In the case of $[(OC)_2(C_3H_5)Mo(\mu-L)FeCp]$ ($L = C_5H_2Me_2C_5H_4, C_9H_6C_5H_4$), the observed voltammograms are similar to those which would be expected from the superposition of two independent electrochemical systems. However, when $L = C_5Me_4C_5H_4$, the oxidation potentials of the monometallic species are close to one another ($[Cp_2Fe]$, $E_{1/2} = +0.54$ V; $[Cp^*Mo(C_3H_5)(CO)_2]$, $E_{1/2} = +0.62$ V). In this case, it appears that the molybdenum center is oxidized first, and thus the consequent withdrawal of electron density from the iron center causes a positive shift in the potential of its oxidation couple.²¹⁶

Similarly, the fulvalene-bridged tungsten–iron complexes have been examined electrochemically, this time for reduction reactions. $[(OC)_3MeW(\mu-C_5H_4C_5H_4)Fe(C_5H_4COMe)]$ displays an irreversible reduction at -2.20 V which is accompanied by a cleavage of the tungsten–methyl bond. The product complex shows a second, reversible reduction process at $E_{1/2} = -2.41$ V, thought to be due to the ferrocenic portion of the molecule. Attempts to further characterize the products by bulk electrolysis yielded few results.²¹⁹

The chromium–iron complexes $[(C_5R_5)Cr(\mu-\eta^5C_r, \eta^3Fe-cot)Fe(CO)_3]$ show reversible oxidation processes at -0.10 V ($R = H$) and -0.20 V ($R = Me$), as well as irreversible oxidations at potential greater than $+0.54$ V. Reduction of these complexes occurs at around -2.5 V: this is reversible for $R = H$ but not for $R = Me$, where an EC process appears to be involved. Replacement of a carbonyl ligand with a phosphine leads to a shift in the oxidation potentials of more than -0.25 V. However, $[(C_5R_5)Cr(\mu-\eta^5C_r, \eta^3Fe-cot)Fe(CO)_2(PF_3)]$ presents a reversible oxidation at -0.15 V, an indication of the high π -acidity of PF_3 .⁶¹

Orth and co-workers have studied the oxidative electrochemistry of a number of molybdenum–platinum complexes.²⁶⁸ The cationic compound $[(OC)_3Mo(\mu-dppm)_2PtH]^+$ shows a reversible couple at $+0.78$ V and an irreversible wave at $+1.82$ V. The first process is assigned to the Mo(0)/Mo(I) couple, in contrast to the irreversible nature of the oxidation of the monomeric precursor $[Mo(CO)_3(\eta^1-dppm)(\eta^2-dppm)]$. In fact, the voltammogram is similar to that of the neutral heterobimetallic species $[(OC)_3Mo(\mu-dppm)_2PtHCl]$ except that the two processes are shifted to potentials 400 mV more positive in the case of the cationic species. The situation is more complex in the molybdenum(II)–platinum(II) complex $[(OC)_2CpMo(\mu-PPh_2)(\mu-H)Pt(PPh_3)(MeCN)]^+$. The *trans*- and *cis*-isomers show separate behaviors, with irreversible waves at $+0.93$ and $+1.12$ V, assigned to Mo(II)/Mo(III) processes, and at $+1.64$ and $+1.81$ V, assigned to Pt(II)/Pt(IV) processes. The Mo(II)/Mo(III) process of the *cis*-isomer occurs at a potential 220 mV more positive than that of the model complex $[(OC)_2CpMo(\mu-PPh_2)(\mu-H)Pt(PPh_3)_2]^+$, while that of the *trans*-isomer is virtually unchanged in potential. The coordination sphere of the molybdenum center is identical in the three complexes, emphasizing the

ability of the metal centers to communicate through the bridging ligands.

The cyclic voltammograms of the fulvalene complexes $[(OC)_3M(\mu-C_5H_4C_5H_4)M'(CO)_2]$ ($M = Mo, W; M' = Fe, Ru$) changed radically on addition of an excess of PMe_3 . The new processes at $E_p = +1.71$ V and $E_p = +0.09$ V are characteristic of the zwitterionic complex $[(OC)_3M^-(\mu-C_5H_4C_5H_4)M'^+(CO)(PMe_3)_2]$. The addition of phosphine is very slow under nonelectrocatalytic conditions. The reaction can also be carried out using $[CpFe(C_6Me_6)]$ as the electrocatalyst. It is thought that the addition of phosphine occurs at a 17-electron late metal center produced by the 1-electron reduction of the starting complex with concomitant cleavage of the metal–metal bond.²²⁰

The tungsten–iron complex $[(OC)_2ClCpW(\mu-Ph_2PC_5H_4)FeMe(CO)_2]$ is not reduced by $NaBH_4$ or by Bu_3SnH but can be reduced by sodium amalgam to an unstable anionic species, which could correspond to the removal of the chloride ligand. Quenching with iodomethane led to the methyltungsten complex $[(OC)_2MeCpW(\mu-Ph_2PC_5H_4)FeMe(CO)_2]$.¹¹²

Reaction of the carboxylate-bridged compound $[Cp_2ClZr(\mu-O_2C-K_{Zr}, O, K_{Zr}, O, K_{Ru}, C)RuCp(CO)_2]$ with 2 equiv of $[Cp_2ZrHCl]$ gives the reduced species $[Cp_2ClZr(\mu-OCH_2-K_{Zr}, O, K_{Ru}, C)RuCp(CO)_2]$. Although this is formally a reduction of the bridging CO_2^- ligand to doubly deprotonated methanol, labeling studies indicate that the new bridging ligand is derived from one of the terminal carbonyls, and that the CO_2^- ligand is transformed into CO .¹⁶⁷

The chemical oxidation of heterobimetallic complexes has also been examined in a small number of systems. Reaction of the 33-electron tantalum–cobalt complex $[Cp_2Ta(\mu-CH_2)_2CoCp]$ with organic disulfides leads to cleavage of the S–S bond, giving the diamagnetic compound $[Cp_2Ta(\mu-CH_2)_2CoCp(SR)]$. The reaction appears to occur by radical attack or outer sphere electron transfer, depending on the electronic character of the disulfide.^{196,269}

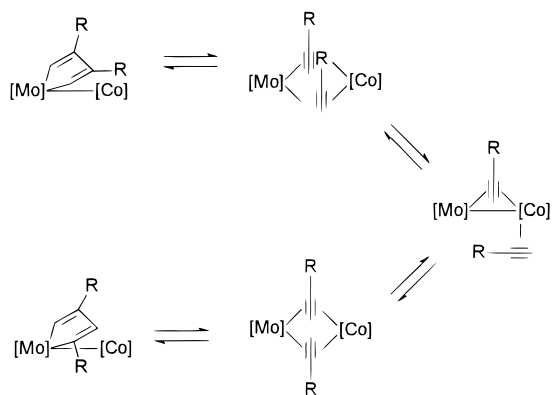
The macrocyclic chloro-bridged vanadium(III)–iron(II) complex $[Fe(entnim)(\mu-Cl)VCl]^+$ (see Figure 51) reacts with 2,4,6-trimethylidosobenzene, O_2 , or $[Cp_2Fe]^+$ to give the vanadium(IV)–iron(II) complex $[Fe(entnim)VO]^{2+}$. Although any of these oxidizing agents would be expected to oxidize an iron(II) center, this is not observed, and the oxidation occurs exclusively at the vanadium center. Analogous behavior is shown by the vanadium(III)–cobalt(II) complex, for which the oxidation of $[Co(entnim)(\mu-Cl)VCl]^+$ gives exclusively $[Co(entnim)VO]^{2+}$.²⁴⁶

Reaction of an excess of trimethylamine *N*-oxide (>5 equiv) with the μ -alkylidene tungsten–palladium complex $[(OC)CpW(\mu-CO)(\mu-CAR_6H_4CH_2NMe_2)PdCl]$ is nonselective, and although the ketone product of the oxidation of the alkylidene bridge was isolated in 77% yield, the organometallic products have not been identified. Using a 2–4-fold excess of Me_3NO allows the isolation in low yield of tungsten-oxidized species in which either the terminal carbonyl or both the carbonyls are replaced by oxo ligands.²⁰¹

E. Isomerization

Reaction of $[CpMoCl(\eta^2-PhC\equiv CMe)_2]$ with $Co_2(CO)_8$ gives the flyover complex $[(OC)_2CpMo(\mu-MeC=$

Scheme 1



CPhCMe=CPh)Co(CO)₂] as the kinetic product. Heating a toluene solution of this compound at 110 °C for 24 h results in quantitative isomerization of the bridging ligand to give the isomer with both CMe groups α to molybdenum (see Scheme 1). When the reaction is carried out in the presence of bis(*p*-tolyl)acetylene, no incorporation of this alkyne is observed, nor any free methylphenylacetylene.²³⁹

Methyl transfer from tungsten to rhodium can be thermally initiated in the fulvalene-bridged system [(OC)₂MeW(μ -C₅H₄C₅H₄)(μ -CO)Rh(CO)], resulting in [(OC)₃W(μ -C₅H₄C₅H₄)RhMe(CO)]. The same complex is also obtained by the thermolytic decarbonylation of [(OC)₃MeW(μ -C₅H₄C₅H₄)Rh(CO)₂].²¹⁷

F. Carbonylation

The complex [(OC)₃W(μ -C₅H₄C₅H₄)RhMe(CO)] is carbonylated at 45 °C under 1 bar of CO to give the acetyl complex [(OC)₃W(μ -C₅H₄C₅H₄)Rh(COMe)(CO)]. This reaction can readily be reversed by refluxing in toluene.²¹⁷

The zirconium–platinum complexes [Cl₂Zr(μ -C₅H₄-PPh₂)₂PtClPh] and {[Cl₂Zr(μ -[C₅H₄)₂PPh]}₂PtClPh] react slowly with CO to give the corresponding benzoylplatinum derivatives. However, the analogous starting complexes with two phenyl ligands attached to platinum are almost inert to CO at room temperature, the only observed minor product arising from the substitution of the metallophosphine by CO.^{109,110}

Although the reaction of *anti*-[(OC)₃Cr(μ -indenyl)-Rh(cod)] with carbon monoxide leads directly to the formation of [(OC)₃Cr(μ -indenyl)Rh(CO)₂], the reaction of the chromium–iridium analogue is somewhat more complex. Carbonylation at –70 °C produces [(OC)₃Cr(μ - η^6 Cr, η^1 Ir-indenyl)Ir(cod)(CO)₂]: the cyclooctadiene ligand is substituted at room temperature to give [(OC)₃Cr(μ - η^6 Cr, η^1 Ir-indenyl)Ir(CO)₄] (see Figure 58). The expected product of the carbonylation, *syn*-[(OC)₃Cr(μ - η^6 Cr, η^1 Ir-indenyl)Ir(CO)₂], was formed independently by the reaction of [Cr(CO)₃(MeCN)₃] with [(η^5 -indenyl)Ir(CO)₂], and crystallographically

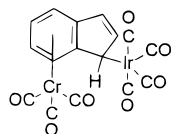


Figure 58. Proposed structure of [(OC)₃Cr(μ -indenyl)Ir(CO)₄]. Redrawn from ref 158.

characterized. The *anti*-isomer, obtained by decarbonylation of [(OC)₃Cr(μ - η^6 Cr, η^1 Ir-indenyl)Ir(CO)₄] on bubbling with argon at room temperature, was unstable and could not be obtained in the solid state. The complex [(OC)₃Cr(μ - η^6 Cr, η^1 Ir-indenyl)Ir(CO)₂(μ -CO)]₂ can be isolated as a precipitate under certain conditions. Redissolution gives [(OC)₃Cr(μ - η^6 Cr, η^1 Ir-indenyl)Ir(CO)(μ -CO)]₂ at low temperature: above 0 °C, the carbonyl bridges between the iridium centers cleave, forming the *anti*-dicarbonyl complex.¹⁵⁸

G. Stoichiometric Hydrogenation of a Sulfur-Containing Compound

Bianchini and co-workers have examined a tungsten–rhodium system as a potential model for heterogeneous catalysts for hydrodesulfurization. The complex [(OC)₅W(μ -SC₆H₄CH=CH₂- κ W, S_{κ Rh}, S_{κ Rh}CH=CH₂)Rh(triphos)] (triphos = HC(CH₂PPh₂)₃) reacts with hydrogen (30 bar) at temperatures of less than 70 °C, leading to the hydrogenation of the coordinated double bond. The product complex [(OC)₄W(μ -H)(μ -SC₆H₄Et)RhH(triphos)] reacts further at higher temperatures with cleavage of the sulfur–carbon bond of the thiolate. The resulting rhodium species is [RhH(CO)(triphos)]: the fate of the tungsten center was not determined.⁷³

H. Trimerization of Allenes

Reaction of allene with [(OC)Cp'Mo(μ -CO)₂NiCp(CO)] appears to lead mainly to the oligomerization of the substrate, but a heterobimetallic complex has been isolated in low yield. An X-ray crystal structure determination showed this to be [(OC)₂Cp'Mo{ μ -(H₂C)₂CCH₂C(=CH₂)C(CH₂)₂}NiCp] (see Figure 41), in which each metal center is η^3 -bound to an allyl moiety. The bridging ligand arises from the trimerization of allene.²¹²

I. Transmetalation

Reaction of [(OC)₃M(μ -C₅H₂Ph₂PPh₂- κ M,C₅H₂Ph₂)(η^5), κ P₄P)PdI(PPh₃)] (M = Mo, W) with Bu₃SnC \equiv CC₆H₄NO₂ leads to elimination of Bu₃SnI and formation of a palladium–carbon bond to the acetylene. This transmetalation reaction is particularly interesting as a model of one of the fundamental steps in palladium-catalyzed metal–carbon bond formation.¹¹⁴

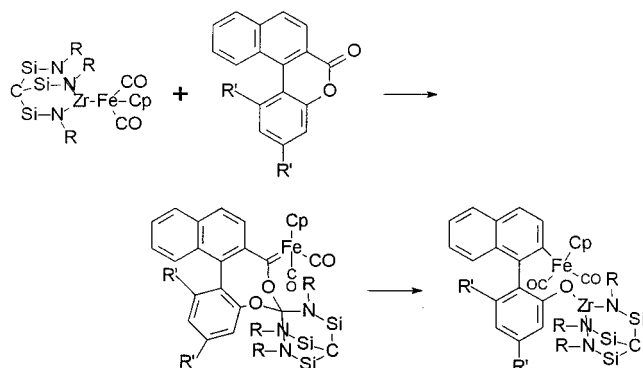
J. Hydride Abstraction

Reaction of Ph₃C⁺ with the propanediyl-bridged compound [(OC)₃CpMo(μ -C₃H₆)FeCp(CO)₂] leads to the removal of a hydrogen atom from the bridging alkyl chain, although exactly which carbon atom is affected is uncertain.²⁰⁷

K. Lactone Ring-Opening

The unbridged zirconium–iron complex [{HC(SiMe₂-NC₆H₄F)₃}ZrFeCp(CO)₂] cleaves the six-membered biaryl lactone C₆H₂R₂OCOC₁₀H₆ (R = Me, OMe) to give the plane chiral bimetallic complex [{HC(SiMe₂-NC₆H₄F)₃}Zr(μ -OC₆H₂R₂C₁₀H₆CO- κ Zr, O_{κ Zr}, O_{κ Fe)CpFeCp(CO)₂] (see Scheme 2). This cooperative reac-

Scheme 2



R = C₆H₄F; R' = Me, OMe

tivity may be of synthetic utility in the preparation of natural products containing a chiral biaryl axis.²⁴¹

L. Stoichiometric Hydrogenation of Alkenes

The zirconium–rhodium complex [Cp*Zr(μ-OCH₂-PPh₂)₂RhH₂(PPh₃)] slowly hydrogenates ethene to ethane, giving [Cp*Zr(μ-OCH₂PPh₂)₂Rh(PPh₃)] as the organometallic product. Although reaction of this compound with H₂ re-forms the dihydride (see section V.B.3), a catalytic process seems difficult to achieve as excess alkene displaces the triphenylphosphine ligand.¹⁴

M. Photochemistry

Irradiation of the chromium–iron complex [(OC)₃Cr(μ-C₆H₅SiMe₂SiMe₂-κ_{Cr}Ph,κ_{Fe}Si)Fe(C₅R₅)(CO)₂] (R = H, Me) leads to decarbonylation and a 1,2-silyl shift to afford the silylidene-bridged species [(OC)₂Cr(μ-C₆H₅SiMe₂-κ_{Cr}Ph,κ_{Fe}Si)(μ-SiMe₂)Fe(C₅R₅)(CO)]. Further irradiation of the Cp* product in the presence of carbon monoxide gives [(OC)₃Cr(μ-C₆H₅SiMe₂-κ_{Cr}Ph,κ_{Fe}Si)FeCp*(CO)₂] (see Scheme 3).¹³³

N. Dissociation of the Bimetallic Framework

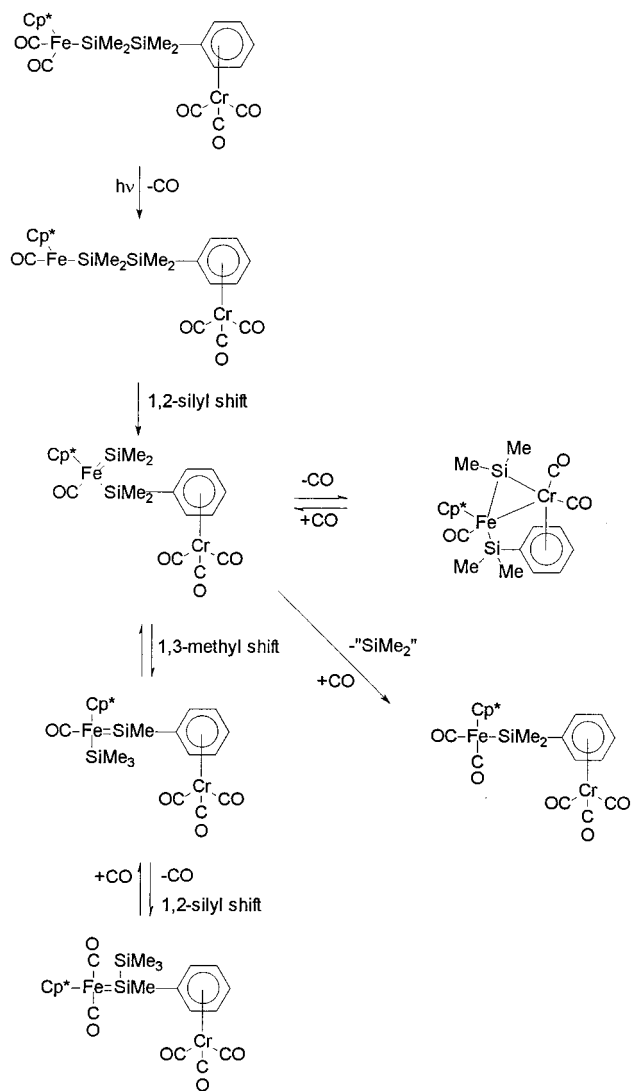
Although many heterobimetallic compounds are relatively unstable, only in a few cases are the mechanisms and products of decomposition well defined.

The η⁶-cycloheptatriene ligand in [(OC)₅Mo(η⁶-Mo,η¹-Ru-C₇H₇)RuCp*(CO)₂] is replaced by three acetonitrile ligands at room temperature, to give [Mo(CO)₃(MeCN)₃] and [Cp*Ru(η¹-C₇H₇)(CO)₂]. The homologous series of complexes [(OC)₃M(μ-η⁶_M,η¹_{M'}-C₇H₇)M'(η⁵-C₅R₅)(CO)₂] (M = Cr, Mo, W; M' = Fe, Ru; R = H, Me) also shows thermal instability. The complexes decompose at room temperature (M' = Fe) or at 100 °C (M' = Ru) to give [M₂(CO)₂(μ-η⁶,η⁶-C₁₄H₁₄)] and [M'₂(C₅R₅)₂(CO)₄].¹²²

The unbridged lutetium–ruthenium bond in [(thf){C₅H₃(SiMe₂)₂}₂LuRuCp(CO)₂] is readily protolyzed by various HX, with the proton remaining on ruthenium and the anionic ligand binding to lutetium. The same reactivity is shown toward other electrophiles, e.g., HgCl₂.²⁵

The reaction of the tungsten–iron compound [(OC)₃CpW(μ-C₆H₁₂)FeCp(CO)₂] with HCl leads to the selective cleavage of the tungsten–carbon bond and

Scheme 3



the formation of [CpWCl(CO)₃] and [CpFe(C₆H₁₃)(CO)₂]. The authors note that tungsten–carbon bonds are thermodynamically more stable than the iron–carbon bonds: their conclusion of the kinetic inertness of the iron–carbon bond should be balanced, in our opinion, by a consideration of the metal–chlorine bond strengths.²⁰⁷

Dissociation of the heterobimetallic framework can also occur by intramolecular ligand transfer. Hence, the transfer of the tetramethylphosphole from ytterbium to ruthenium in [(C₃N₂Me₂'Pr₂)Yb(μ-C₄PMe₄-κ_{Yb}C₄P(η⁵),κ_{Ru}P)RuH₂(PPh₃)₂] leads to the cleavage of the complex, with [RuH(η⁵-C₄PMe₄)(PPh₃)₂] as the isolated product.¹⁷⁵

Intramolecular reductive elimination has also been noted in the complex [Cp₂Ti(μ-Cl)(μ-CH₂)PdMe(PMe₃)]. This leads to the formation of [Cp₂TiClEt] and an unstable palladium(0) species. The latter can be trapped by carrying out the reaction in the presence of 3-chloro-2-methylpropene (methallyl chloride), leading to the isolation of [PdCl(C₃H₄Me)(PMe₃)] as the final palladium-containing product.¹⁹⁰

Finally, Shyu and co-workers have studied the decomposition of [(OC)₃CpWCo(CO)₄] under vacuum MOCVD conditions with the aim of retaining the

bimetallic nature of the starting complex, that is to say, a film with a tungsten/cobalt ratio of 1. This is possible with decomposition temperatures up to 300 °C: higher temperatures lead to cobalt-rich films ($W/Co = 0.5$ at 500 °C). The films are rich in carbon (ca. 40 atom %), but this contamination is removed by heating under oxygen at 900 °C, giving polycrystalline films of $WCoO_4$.²⁷⁰

VI. Catalytic Activity

Despite the numerous preparative and structural studies of early-late heterobimetallic complexes, and the fact that many of these unite metal centers which, in isolation, would be expected to show catalytic activity, investigations of this type of reactivity are remarkably scarce.

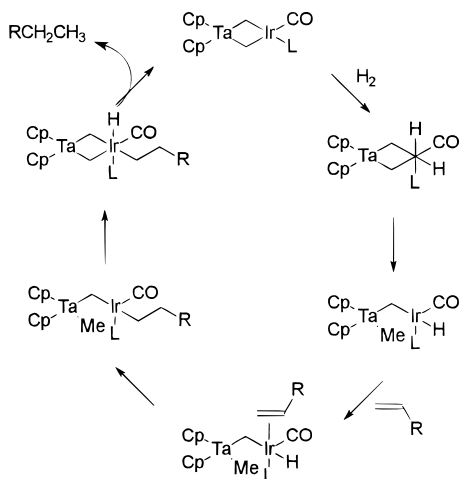
A. Hydrogenation

1. Hydrogenation of Alkenes

The tantalum-iridium complex $[Cp_2Ta(\mu-CH_2)_2Ir(CO)L]$ ($L = CO, PPh_3$) is a catalyst for alkene hydrogenation. The rate of hydrogenation shows first-order dependence in the complex, hydrogen, and alkene. When the reaction is carried out with D_2 , incorporation of deuterium into the bridging methylene groups is observed with a rate higher than that of alkene hydrogenation. Analogous monometallic complexes were prepared in which the tantalum-centered portion of the molecule was replaced by a phosphorus ylide to give $[R_2P(CH_2)_2Ir(CO)L]$ ($R = Me, Ph$): although these appear to have a similar electron density on the iridium center (as shown by IR and ^{31}P NMR), they are up to 150 times slower as alkene hydrogenation catalysts. Significantly, no deuterium incorporation into the methylene bridges of the phosphorus ylide complexes was observed.^{193,262}

The mechanism proposed for the reaction is shown in Scheme 4. The most notable feature is that the necessary vacant coordination site is formed not by ligand dissociation but by the reductive elimination of a methyl group which remains bound to tantalum. This reductive elimination is fully reversible, and no fragmentation of the bimetallic compound is observed. The presence of the tantalum center is

Scheme 4

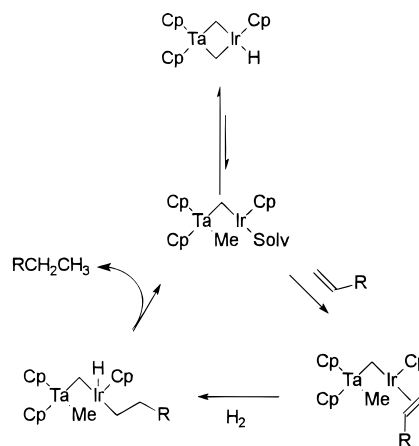


indispensable for this mechanism, which does not appear to occur in the complexes of phosphorus ylides.²⁶²

The analogous tantalum-rhodium complexes also catalyze alkene hydrogenation much more rapidly than the tantalum-iridium complexes. Substitution of hydrogen by deuterium in the bridge also occurs, but in this case it is slower than alkene hydrogenation. Complexes of phosphorus ylides catalyze the hydrogenation reaction with the same activity as the tantalum-rhodium complexes, and there is no evidence for a specific role of the early metal in this case.^{193,262}

A similar tantalum-iridium complex, $[Cp_2Ta(\mu-CH_2)_2IrHCp^*]$, is also a catalyst for alkene hydrogenation. However, the mechanism appears to be somewhat different. In particular, deuterium incorporation into the methylene bridges occurs only at 105 °C, and then rather slowly. Also, the catalysis is completely inhibited by addition of PMe_3 , even though no reaction can be observed between the starting complex and the phosphine. This inhibition is reversible on recrystallization of the complex. Butts and Bergman have proposed that the starting complex decomposes to a small extent under hydrogenation conditions, giving a highly active catalytic species. However, they are forced to assume that this decomposition occurs to the same extent in each of their repeated experiments. In our view, this is more consistent with an equilibrium than with irreversible decomposition. We propose the mechanism shown in Scheme 5. The first step is reductive elimination of

Scheme 5



the methyl group: unlike in the complexes above, this can occur without prior oxidative addition of hydrogen. Indeed, oxidative addition of H_2 to the starting complex would lead to a highly sterically hindered iridium trihydride. The hydrogenation cycle then proceeds classically on the iridium center. Phosphine inhibition occurs by blocking the vacant site: the fact that the phosphine adduct cannot be observed is an indication of the extremely low concentration of the active species.¹⁹⁵

2. Hydrogenation of Ketones

He et al. have examined the activity of a number of phosphido-bridged bimetallic complexes $[(OC)_4M-$

$(\mu\text{-PPh}_2)_2\text{Ru}(\text{CO})_3$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) and $[(\text{OC})_4\text{M}(\mu\text{-PPh}_2)_2\text{M}'(\text{PPh}_3)]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}; \text{M}' = \text{Pd}, \text{M} = \text{Mo}, \text{W}; \text{M}' = \text{Pt}$) for the hydrogenation of cyclohexanone (140 °C, 40 bar of H_2 , 23 h). The best results were obtained for $[(\text{OC})_4\text{M}(\mu\text{-PPh}_2)_2\text{Ru}(\text{CO})_3]$ (56%, $\text{M} = \text{Mo}$; 21%, $\text{M} = \text{Cr}$), but the yields are still somewhat disappointing. The other complexes were virtually or completely inactive.⁹⁰

B. Hydroformylation of Alkenes

The phosphido-bridged zirconium–rhodium complex $[\text{Cp}_2\text{Zr}(\mu\text{-PPh}_2)_2\text{Rh}(\text{CO})(\text{PPh}_3)]$ has been shown to be a moderately active catalyst precursor for the hydroformylation of 1-hexene at 25 °C and 1 bar of H_2/CO . It is somewhat less active than $[\text{Rh}(\text{CO})(\text{PPh}_3)_3]$ (0.9 h^{-1} against 7.3 h^{-1}) but shows a high specificity for *n*-heptanal (94% against 69%). The precursor is recovered in virtually quantitative yield from the reaction mixture after catalysis.⁸⁰

The more flexible metallocphosphines $[(\text{C}_5\text{H}_4\text{R})_2\text{Zr}(\text{CH}_2\text{PPh}_2)_2]$ ($\text{R} = \text{H}, \text{'Bu}$) have also been used as catalyst modifiers. In the well-characterized systems $[(\text{C}_5\text{H}_4\text{R})_2\text{Zr}(\mu\text{-CH}_2\text{PPh}_2)_2\text{Rh}(\text{cod})]^+$ and $[(\text{C}_5\text{H}_4\text{R})_2\text{Zr}(\mu\text{-CH}_2\text{PPh}_2)_2\text{Rh}_2(\text{S}'\text{Bu})_2(\text{CO})_2]$, the bimetallic complexes display lower rates and lower selectivities than the monometallic analogues $[\text{Rh}(\text{cod})(\text{PPh}_3)_2]^+$ and $[\text{Rh}_2(\mu\text{-S}'\text{Bu})_2(\text{CO})_2(\text{PPh}_3)_2]$.¹³⁸ However, when $[\text{Cp}_2\text{Zr}(\text{CH}_2\text{PPh}_2)_2]$ is used as a modifier for $[\text{RhH}\{\text{P}(\text{OPh})_3\}_4]$ or $[\text{RhH}(\text{CO})\{\text{P}(\text{OPh})_3\}_3]$, the yields are equivalent to those obtained using PPh_3 or *dppe* and the selectivities in linear aldehyde are greatly increased.²⁷¹ Active catalytic systems have also been formed in situ from $[\text{Rh}(\text{acac})(\text{CO})_2]$ and $[\text{Cp}_2\text{Zr}(\text{CH}_2\text{PPh}_2)_2]$ or $[\text{Cp}_2\text{ZrH}(\text{CH}_2\text{PPh}_2)]$. These systems yield unsaturated monoaldehydes from the hydroformylation of α,ω -dienes, as opposed to the dialdehydes formed by catalysis using $[\text{Rh}(\text{acac})(\text{CO})_2]/\text{PPh}_3$.¹³⁹

The phosphido-bridged compounds $[(\text{OC})_4\text{M}(\mu\text{-PPh}_2)_2\text{Ru}(\text{CO})_3]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) and $[(\text{OC})_4\text{M}(\mu\text{-PPh}_2)_2\text{M}'(\text{PPh}_3)]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}; \text{M}' = \text{Pd}, \text{M} = \text{Mo}, \text{W}; \text{M}' = \text{Pt}$) are very poor catalysts for the hydroformylation of styrene (120 °C, 20 bar, 23 h), with only the tungsten–ruthenium (10%) and tungsten–palladium (15%) complexes showing a significant conversion. The selectivities for the branched product were less than 70%.⁹⁰ However, Gelmini and Stephan have reported that $[\text{Cp}_2\text{Zr}(\mu\text{-PPh}_2)_2\text{Rh}(\text{CO})(\text{PPh}_3)]$ gives a higher selectivity (94%) for 1-heptanal than $[\text{Rh}(\text{CO})(\text{PPh}_3)_3]$ (69%) in the hydroformylation of 1-hexene (25 °C, 1 bar, 100 h), albeit for a slightly reduced activity (91% conversion, compared with 99%).⁸⁰ Larsson et al. obtained similar results using the trimethylsilyl-substituted compound $[(\text{C}_5\text{H}_4\text{-SiMe}_3)_2\text{Zr}(\mu\text{-PPh}_2)_2\text{Rh}(\text{CO})(\text{PPh}_3)]$, but found the trimeric complex $\{[(\text{C}_5\text{H}_4\text{-SiMe}_3)_2\text{Zr}(\mu\text{-PPh}_2)_2]_2\{\text{Rh}_2(\text{S}'\text{Bu})_2\}$ to have only a very low activity.⁷⁹

The tungsten–rhodium complex $[(\text{OC})_4\text{W}(\mu\text{-PPh}_2)_2\text{Rh}(\text{CO})(\text{PPh}_3)]$ has been studied as a hydroformylation catalyst for a number of substrates.²⁷² It showed a very high selectivity for the branched aldehyde (98%) in the hydroformylation of styrene (50 °C, 26 bar of H_2/CO) with quantitative conversion in 20 h. Hydroformylation of vinyl acetate gave a relatively high yield of aldehyde (72% in 20 h), but with a

disappointing selectivity for the branched aldehyde (75%). Allyl acetate gave an 89% selectivity for the linear aldehyde with a 70% isolated yield. Phosphinoalkenes were also hydroformylated, with selectivities almost identical to those obtained with monometallic rhodium-based catalysts. The products of stoichiometric reactions between phosphinoalkenes and the tungsten–rhodium complex have also been characterized.²⁷³

C. Cyclotrimerization of Alkynes

The indenyl-bridged chromium–rhodium complexes $[(\text{OC})_3\text{Cr}(\mu\text{-indenyl})\text{Rh}(\text{CO})_2]$, in which the indenyl bridge may be methylated or not, are between 7 and 70 times faster as catalysts for the cyclotrimerization of alkynes to substituted benzenes than $[(\eta^5\text{-indenyl})\text{Rh}(\text{cod})]$.^{150,153} The catalysis is exclusively due to the *trans*-isomer. A temperature-dependent induction period is observed during the cyclotrimerization of dimethyl butynedioate (dimethyl acetylenedicarboxylate), and this is thought to be due to the need to substitute both the carbonyl ligands on rhodium by alkyne to produce the active catalytic species. Hydrogenation of the alkyne to dimethyl *trans*-butenedioate (dimethyl fumarate) is observed to a small extent, and this may play a role in the substitution of the second carbonyl ligand.²⁷⁴ The increased activity of these complexes compared to other (indenyl)rhodium species is thought to be due to the lower barrier for ring slippage between η^5 - and η^3 -forms. Such ring slippage is commonly invoked to explain the increased reactivity of η^5 -indenyl complexes compared to their cyclopentadienyl analogues.²⁷⁵

D. Oxidation of Alcohols

To overcome some of the difficulties of chromate oxidation in organic chemistry, Shapley and co-workers have examined the chemistry of the chromium–osmium heterobimetallic anions $[\text{O}_2\text{Cr}(\mu\text{-O})_2\text{Os}(\equiv\text{N})\text{R}_2]^-$ ($\text{R} = \text{Me}, \text{CH}_2\text{SiMe}_3$). These compounds selectively catalyze the oxidation of primary and secondary alcohols by atmospheric oxygen. Primary alcohols are oxidized to aldehydes with no carboxylic acid formation, and carbon–carbon double bonds are unaffected.¹⁸² Although these compounds do not react with PPh_3 , they react slowly with *dppe* and catalyze its oxidation by atmospheric O_2 .¹⁸³

E. Direct Carbonylation of Ethene

The direct carbonylation of ethene to acrolein is catalyzed by the zirconium–rhodium complex $[\text{Cp}^*\text{-Zr}(\mu\text{-S})_2\text{Rh}(\text{CO})_2]^-$ in the presence of excess PPh_3 . The equilibrium lies slightly to the side of the reactants, but addition of triethyl orthoformate displaces it by formation of the acetal. Under the conditions used (140 °C, 20 bar of $\text{CO}/\text{C}_2\text{H}_4$), two turnovers were observed in 16 h. Binuclear rhodium complexes are completely inactive for this reaction, while $[\text{Cp}^*\text{-Zr}(\text{SH})_2]$ gives a small amount of acrolein but rapidly decomposes. Hence, the rhodium center appears to stabilize an active zirconium center, although the

mechanism of the reaction has not been determined.¹⁸⁶

F. Polymerization of Alkenes

The phosphido-bridged complex $[\text{Cp}_2\text{Zr}\{\mu\text{-P}(\text{SiMe}_3)_2\}_2\text{Ni}(\text{CO})_2]$ is a catalyst precursor for the polymerization of ethylene. An activity of 7.46×10^5 g mol⁻¹ atm⁻¹ h⁻¹ (grams of polymer per mole of catalyst per atmosphere of ethylene per hour) was reported at 25 °C and in the presence of 1350 equiv of methylaluminoxane (MAO).⁸¹

G. Hydrosilylation of Alkenes

The tantalum–iridium complex $[\text{Cp}_2\text{Ta}(\mu\text{-CH}_2)_2\text{Ir}(\text{CO})_2]$ (see section VI.A) is a catalyst for alkene hydrosilylation. The mechanism is slightly different for that proposed for alkene hydrogenation. The first step is the reversible oxidative addition of the Si–H bond to the iridium center. Although reversible reductive elimination of the methylene bridge does occur, as shown by H/D exchange, the vacant site for alkene coordination is thought to be produced primarily by CO dissociation. β -Hydride insertion and reductive elimination of the organosilane complete the catalytic cycle.²⁶³ Unlike other hydrosilylation catalysts,²⁷⁶ only very small quantities of vinylsilanes are produced, the main product of the hydrosilylation of ethene being SiEt₄.

H. Isomerization of Alkenes

As might be expected, the alkene hydrogenation and hydrosilylation catalysts $[\text{Cp}_2\text{Ta}(\mu\text{-CH}_2)_2\text{M}(\text{CO})\text{L}]$ (M = Rh, Ir; L = CO, PPh₃) also catalyze the isomerization of higher alkenes.¹⁹³ The kinetics of the isomerization are consistent with a β -elimination process from an hydridoalkyl intermediate in a hydrogenation or hydrosilylation cycle.²⁶²

VII. Conclusion

The number and the variety of early–late hetero-bimetallic complexes described in the literature continue to grow rapidly. Over the last 10 years, more and more effort has been devoted to the investigation of the reactivity of these complexes, although the majority have yet to be studied in any detail. The systematic study of the catalytic activity of these compounds is still in its infancy. The studies which have been carried out indicate that the reactivity of early–late bimetallic complexes can be strikingly different from that of their monomeric analogues. This altered reactivity may or may not be due to direct metal–metal interactions: theoretical studies indicate that, in many cases, these interactions are very weak. The description and understanding of the reactivity of these compounds is obviously still a field ripe for future work.

VIII. Abbreviations

con	cyclooctene
cot	cyclooctatetraene
Cp'	methylcyclopentadienyl
dippe	1,2-bis(diisopropylphosphino)ethane

dmb	2,3-dimethylbutadiene
dmpe	1,2-bis(dimethylphosphino)ethane
dpae	1-(diphenylarsino)-2-(diphenylphosphino)-ethane
dppp	1,3-bis(diphenylphosphino)propane
H ₂ entnim	bis[(2-pyridylmethyl){(2-hydroxy-3-formyl-5-methylphenyl)methyl}amino]ethane
Hhfacac	1,1,1,5,5,5-hexafluoropentane-2,4-dione
Hpyphos	6-(diphenylphosphino)-2-pyridone
H ₂ teta	triethylenetetramine, 1,4,7,10-tetraazadecane
tfbb	tetrafluorobenzobarrelene, tetrafluorobenzocyclopentadiene, [5,6]bicyclo[2.2.2]octa-2,5,7-triene
TfOH	trifluoromethanesulfonic acid
Tol	<i>p</i> -tolyl
Tp*	tris(3,5-dimethylpyrazolyl)borate

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