

Cycloheptatriene and -enyl Complexes of the Early Transition Metals

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I. Abbreviations

COD	1,5-cyclooctadiene
Cy	cyclohexyl
dippe	1,2-bis(diisopropylphosphino)ethane
dme	1,2-dimethoxyethane
dmpe	1,2-bis(dimethylphosphino)ethane
dppe	1,2-bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
en	ethylenediamine
Fc	ferrocene
HOMO	highest occupied molecular orbital
LUMO	lowest unoccupied molecular orbital
MO	molecular orbital
MVS	metal vapor synthesis
PE	photoelectron
r.t.	room temperature
SCE	saturated calomel electrode
TCNE	tetracyanoethylene

TCNQ	7,7,8,8-tetracyanoquinodimethane
THF	tetrahydrofuran
tmeda	<i>N,N,N',N'</i> -tetramethylethylenediamine

II. Introduction

The η -cyclopentadienyl (η^5 -C₅R₅) and η -arene (η^6 -C₆R₆) groups are among the most common classes of ligand encountered in organotransition metal chemistry. Transition metal complexes with these ligands have been studied extensively and many of which have contributed to the development of areas such as homogeneous catalysis,¹ organic synthesis,² new materials,³ and biological and medical sciences.⁴ Although cycloheptatriene (η^6 -C₇H₈) and cycloheptatrienyl (η^7 -C₇H₇) transition metal complexes have been known for over three decades, surprisingly, the chemistry of these ligands has been studied little in comparison with that of cyclopentadienyl and arene ligands.

The first η^6 -cycloheptatriene complex, Mo(η^6 -C₇H₈)(CO)₃, was prepared by Wilkinson *et al.* in 1958,⁵ and the first η^7 -cycloheptatrienyl complex, [Mo(η^7 -C₇H₇)(CO)₃][BF₄], was synthesized shortly after.⁶ The early developments of the chemistry of η -C₇-ring transition metal compounds has been reviewed by Deganello, up to the late 1970s.⁷ At that time, cycloheptatriene and -enyl complexes of the group 4 and 5 metals were rare and confined mainly as the sandwich complexes M(η^7 -C₇H₇)(η^5 -C₅H₅) (M = Ti, Zr, V, or Nb), M(η^7 -C₇H₇)(η^5 -C₇H₉) (M = Ti or V), V(η^6 -C₇H₈)₂, and [V(η^7 -C₇H₇)₂]²⁺, and the metal carbonyl V(η^7 -C₇H₇)(CO)₃. For the group 6 metals, in particular, molybdenum, ready accessibility of several precursors, such as M(η^6 -C₇H₈)(CO)₃ (M = Cr, Mo, or W), [M(η^7 -C₇H₇)(CO)₃]⁺ (M = Cr, Mo, or W), M(η^7 -C₇H₇)(CO)₂X (M = Mo or W; X = halides), and [Mo(η^7 -C₇H₇)(η^6 -C₆H₅Me)]⁺, led to a wider range of complexes.

During the past decade more convenient synthetic pathways to several key compounds have been developed; more compounds have been synthesized and structurally characterized and a deeper understanding on the bonding of η^7 -cycloheptatrienyl transition metal complexes has been realized with the aid of photoelectron spectroscopy. The purpose of this review is to provide an overview of the current status in this field of research and to stimulate further research.

In this article, only η^6 -cycloheptatriene and η^7 -cycloheptatrienyl complexes of the group 4, 5, and 6



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transition metals will be reviewed. For the late transition metals, complexes with lower hapticity are dominant and will not be covered. Complexes with cycloheptatriene derivatives such as tropone, heptafulvene, azulene, heptalene, and sesquifulvalene will also be excluded. This review covers work published from 1980 up to mid-1994. Only a selection of the work described in the earlier review⁷ is included in this article.

III. Synthetic Methods

Synthetic routes to η^6 -cycloheptatriene and η^7 -cycloheptatrienyl metal complexes can be broadly classified according to the class of starting material, namely, from metal carbonyls, from metal atoms, and from metal chlorides. Specialty and unique routes are presented at the end of this section.

A. From Metal Carbonyls

A traditional method for the preparation of cycloheptatriene complexes involves the displacement of carbonyl groups of homoleptic metal hexacarbonyls by a cycloheptatriene ligand giving $M(\eta^6\text{-C}_7\text{H}_8)(\text{CO})_3$, where $M = \text{Cr}, \text{Mo},$ or W . This method works very well for chromium and molybdenum,^{5,8} but for tungsten, it is much more convenient to first prepare the tris(alkanenitrile)s $\text{W}(\text{RCN})_3(\text{CO})_3$ ($\text{R} = \text{Me},^9 \text{Et},$ or Pr^{10}). The η -cycloheptatriene complexes undergo hydride abstraction readily giving the corresponding η -cycloheptatrienyl complexes (Scheme 1).^{6,9,11}

Recently, this method has been extended to the preparation of substituted cycloheptatriene and -enyl complexes.¹² Thus, treatment of $\text{Mo}(\text{CO})_6$ with 1,3,5,7-tetramethylcycloheptatriene in refluxing octane gives the expected $\text{Mo}(\eta^6\text{-C}_7\text{H}_4\text{Me}_{4-1,3,5,7})(\text{CO})_3$ (**1**) together with the isomers $\text{Mo}(\eta^6\text{-C}_7\text{H}_4\text{Me}_{4-1,2,4,6})(\text{CO})_3$ (**2**) and $\text{Mo}(\eta^6\text{-C}_7\text{H}_4\text{Me}_{4-1,3,4,6})(\text{CO})_3$ (**3**). The latter two complexes arise as a result of sequential 1,5-shifts of the 7-*endo*-hydrogen atom of the initially formed **1** (see section VI.A.1). The inseparable mixture of **2** and **3**, upon treatment with Ph_3C^+ , affords the cycloheptatrienyl cation $[\text{Mo}(\eta^7\text{-C}_7\text{H}_3\text{Me}_{4-1,2,4,6})(\text{CO})_3]^+$ (**4**). However, the same reaction with compound **1** gives **4** in only moderate yield even under more vigorous conditions. Probably, the 7-*exo*-methyl group of **1** hinders the approach of the bulky Ph_3C^+ cation (Scheme 2).

Treatment of $\text{V}(\text{CO})_6$ with cycloheptatriene gives the cycloheptatrienyl complex $\text{V}(\eta^7\text{-C}_7\text{H}_7)(\text{CO})_3$ directly.¹³ Several monosubstituted cycloheptatrienyl vanadium complexes $\text{V}(\eta^7\text{-C}_7\text{H}_6\text{R})(\text{CO})_3$ (where $\text{R} = \text{Me}, \text{Ph}, \text{CN}, \text{OMe}, \text{OPr},$ or CO_2Et) can also be prepared by this method.¹⁴

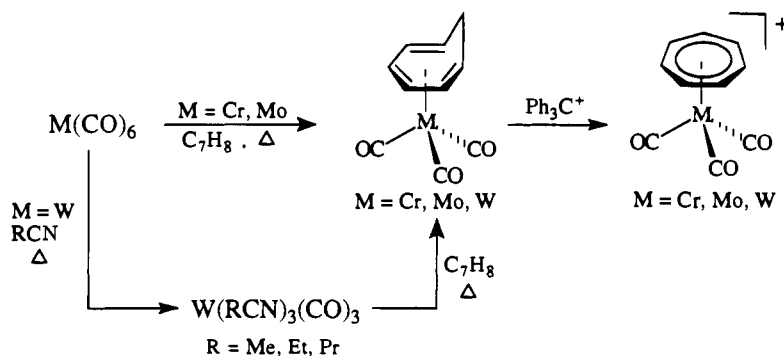
B. From Metal Atoms

Metal vapor synthesis (MVS) has been proved to be a versatile method for the preparation of low-valent metal complexes.¹⁵ Many complexes which as yet cannot be prepared by other methods can be synthesized by means of cocondensation techniques. This method has been used to prepare the compounds $\text{M}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_7\text{H}_9)$, where $\text{M} = \text{Ti},^{16} \text{Zr},^{17} \text{Hf},^{17} \text{V},^{16} \text{Cr},^{18} \text{Mo},^{19}$ or $\text{W},^{19}$ by cocondensation of the metal atoms with cycloheptatriene (Scheme 3).

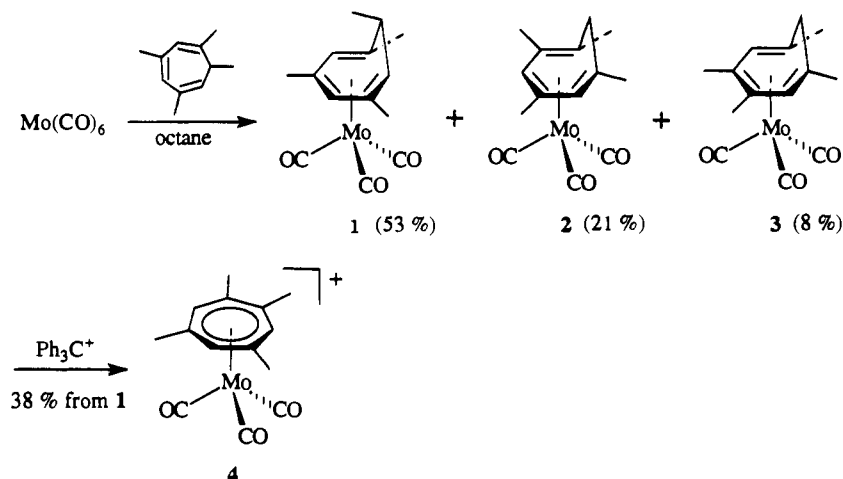
Cocondensation of zirconium or hafnium atoms with cycloheptatriene gives an ill-defined red solid with a stoichiometry close to $\text{M}(\text{C}_7\text{H}_8)_3$. Vacuum pyrolysis at 120–160 °C followed by recrystallization of the red sublimes affords pure $\text{M}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_7\text{H}_9)$ ($\text{M} = \text{Zr}$ or Hf) in 15–20% yield.¹⁷

It was reported that, when a solution of cycloheptatriene in hexane or methylcyclohexane is cocondensed with chromium vapor, the only isolable product is $\text{Cr}(\eta^7\text{-C}_7\text{H}_7)(\eta^4\text{-C}_7\text{H}_{10})$.^{16,20} However, when

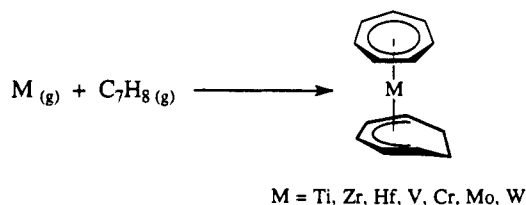
Scheme 1



Scheme 2



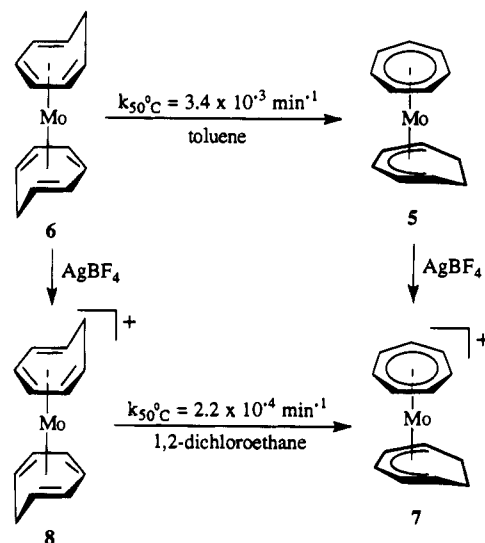
Scheme 3



neat cycloheptatriene is used, the reaction gives $Cr(\eta^7-C_7H_7)(\eta^5-C_7H_9)$ in 45% yield with only a small amount of $Cr(\eta^7-C_7H_7)(\eta^4-C_7H_{10})$.¹⁸

The reaction between molybdenum atoms and cycloheptatriene was originally reported by Skell *et al.* to give $Mo(\eta^7-C_7H_7)(\eta^5-C_7H_9)$ (**5**).¹⁹ However, a reexamination of this reaction by Green *et al.*, including a low-temperature isolation procedure, showed that the thermally sensitive bis(triene) compound $Mo(\eta^6-C_7H_8)_2$ (**6**) was formed in good yields. This compound proved to be unstable over long periods of time or on heating and rearranged cleanly via hydrogen migration to the more stable **5**.²¹ Both **5** and **6** can be oxidized by $AgBF_4$ to give the corresponding cations $[Mo(\eta^7-C_7H_7)(\eta^5-C_7H_9)]^+$ (**7**) and $[Mo(\eta^6-C_7H_8)_2]^+$ (**8**). The latter cation **8** also rearranges to the former cation **7** but the rate is slower than their neutral analogs, as is consistent with the activation energy difference of 14 ± 3 kJ/mol (Scheme 4). Thermal rearrangement of mixtures of **6** and $[D_{16}]$ -**6** gives only **5** and $[D_{16}]$ -**5**; no H/D crossover could be detected by mass spectrometry. Similar results were obtained for the conversion of mixtures of **8** and $[D_{16}]$ -**8**. These

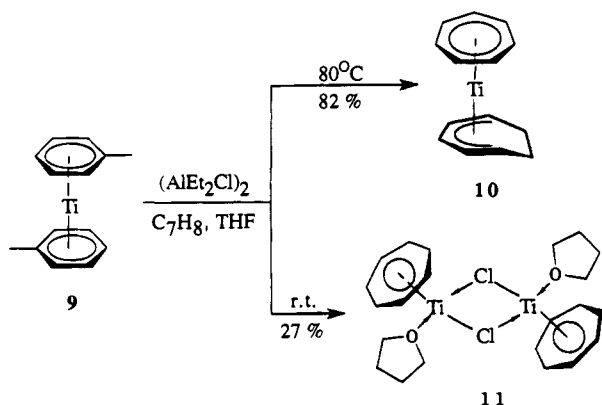
Scheme 4



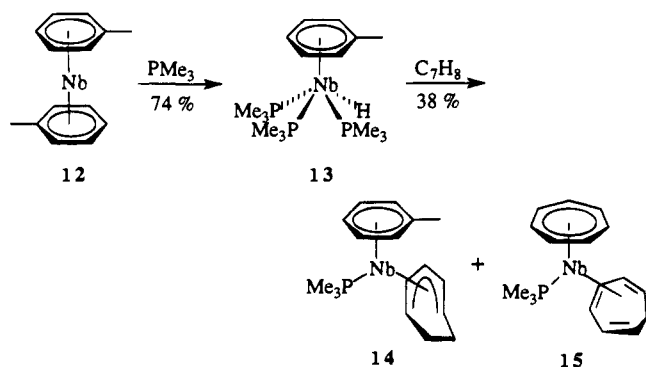
experiments together with the kinetic studies showed that the rearrangements are intramolecular.²¹

The MVS technique also provides indirect routes to cycloheptatriene and -enyl metal complexes. For example, the sandwich compound $Ti(\eta^6-C_6H_5Me)_2$ (**9**), which is readily available from MVS, reacts with a mixture of $(AlEt_2Cl)_2$ and a 2-fold excess of cycloheptatriene in THF at 80 °C for 2 h giving $Ti(\eta^7-C_7H_7)(\eta^5-C_7H_9)$ (**10**) in good yield. However, when the reaction is carried out at room temperature over a period of weeks, with the minimum quantity of solvent and $(AlEt_2Cl)_2$, together with a considerable

Scheme 5



Scheme 6



excess of cycloheptatriene, the crystallographically characterized dimer $[\text{Ti}(\eta^7\text{-C}_7\text{H}_7)(\text{THF})(\mu\text{-Cl})]_2$ (**11**) can be isolated in *ca.* 30% yield (Scheme 5). This dimer, upon treatment with an excess of cycloheptatriene and $(\text{AlEt}_2\text{Cl})_2$ in THF at 80°C , converts to **10**. Thus it appears that **11**, or a related species, such as $\text{Ti}(\eta^7\text{-C}_7\text{H}_7)(\text{THF})_2\text{Cl}$, is an intermediate in the formation of **10** from **9**.²²

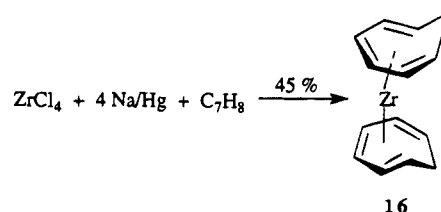
As another example, the sandwich compound $\text{Nb}(\eta^6\text{-C}_6\text{H}_5\text{Me})_2$ (**12**) prepared by MVS reacts with trimethylphosphine giving the half-sandwich compound $\text{Nb}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{PMe}_3)_3\text{H}$ (**13**). Heating a solution of **13** with cycloheptatriene yields a mixture of $\text{Nb}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\eta^5\text{-C}_7\text{H}_9)(\text{PMe}_3)$ (**14**) and $\text{Nb}(\eta^7\text{-C}_7\text{H}_7)(\eta^4\text{-C}_7\text{H}_8)(\text{PMe}_3)$ (**15**) in 1:2 ratio (Scheme 6).²³

C. From Metal Chlorides

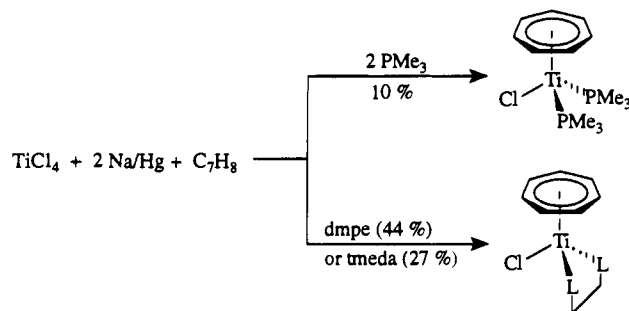
Reduction of metal halides in the presence of olefins is a commonly used method to prepare low-valent metal (π -olefin) complexes. Recently, this method has been used to prepare several key compounds which can generate a wide range of cycloheptatriene and -enyl complexes of the group 4, 5, and 6 metals. These synthetic pathways thus represent direct and convenient entries to these classes of compounds.

Reduction of ZrCl_4 with sodium amalgam in the presence of cycloheptatriene at $< -10^\circ\text{C}$ leads to the rare formally zerovalent zirconium complex $\text{Zr}(\eta^6\text{-C}_7\text{H}_8)_2$ (**16**) (Scheme 7), which is a reactive precursor toward new organometallic compounds of zirconium. When this reaction is carried out at room temperature, an inseparable mixture of **16** and $\text{Zr}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_7\text{H}_9)$ (**17**) is formed. Similarly, reduction of TiCl_4

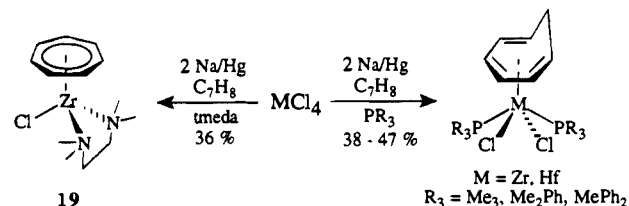
Scheme 7



Scheme 8



Scheme 9

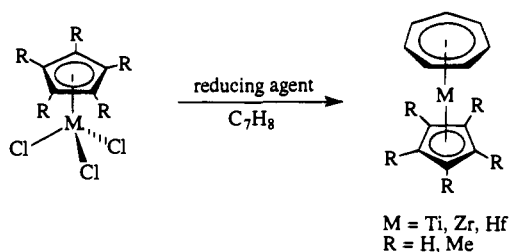


with magnesium turnings in the presence of cycloheptatriene gives a *ca.* 4:1 mixture of the bis(triene) compound $\text{Ti}(\eta^6\text{-C}_7\text{H}_8)_2$ (**18**) and $\text{Ti}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_7\text{H}_9)$ (**10**). Solutions of **18** readily decompose to **10** and it is not possible to isolate pure **18**.²⁴ This reaction is closely analogous to the previous route to compound **10** using isopropylmagnesium bromide as reducing agent.²⁵

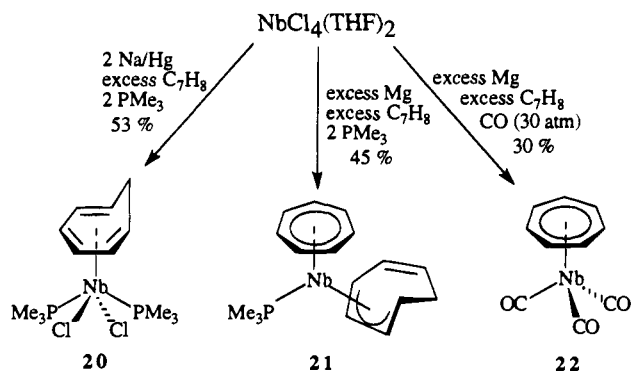
Treatment of TiCl_4 with 2 equiv of sodium amalgam, an excess of cycloheptatriene, and 1 equiv of L_2 [$\text{L}_2 = \text{dmpe}$, tmeda , or $(\text{PMe}_3)_2$] gives the half-sandwich compounds $\text{Ti}(\eta^7\text{-C}_7\text{H}_7)\text{L}_2\text{Cl}$ in a one-pot reaction (Scheme 8).²⁶ The reaction of ZrCl_4 with tmeda under similar conditions generates the zirconium analog $\text{Zr}(\eta^7\text{-C}_7\text{H}_7)(\text{tmeda})\text{Cl}$ (**19**).²⁶ The reaction with tertiary phosphine ligands, however, gives the cycloheptatriene complexes $\text{Zr}(\eta^6\text{-C}_7\text{H}_8)(\text{PR}_3)_2\text{Cl}_2$ in moderate yields and these reactions can be extended to hafnium (Scheme 9).^{27,28} The chemistry of divalent complexes of zirconium and hafnium is relatively unexplored. This reductive method provides a convenient way to prepare these novel compounds in multigram quantities.

The mixed-sandwich complexes $\text{M}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_5\text{R}_5)$ ($\text{M} = \text{Ti, Zr, or Hf}$; $\text{R} = \text{H or Me}$) can also be prepared by a reductive method. Treatment of cyclopentadienylmetal chlorides $\text{M}(\eta^5\text{-C}_5\text{R}_5)\text{Cl}_3$ with appropriate reducing agents, such as magnesium, aluminum, zinc, or isopropylmagnesium bromide, in the presence of cycloheptatriene gives the corresponding sandwich compounds in low (for $\text{M} = \text{Hf}$) to moderate (for $\text{M} = \text{Ti or Zr}$) yields (Scheme 10).²⁹⁻³³ The reaction may be promoted with a small amount of FeCl_3 .³⁴

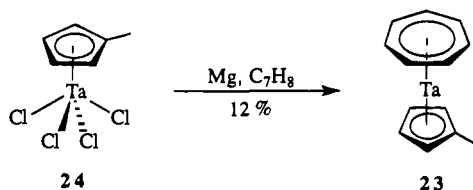
Scheme 10



Scheme 11



Scheme 12

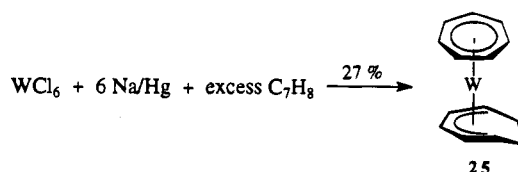


Related reactions on niobium have also been studied. The reduction of $\text{NbCl}_4(\text{THF})_2$ with sodium amalgam or magnesium turnings in the presence of cycloheptatriene and other ligands, such as PMe_3 or CO , gives the compounds $\text{Nb}(\eta^6\text{-C}_7\text{H}_8)(\text{PMe}_3)_2\text{Cl}_2$ (**20**), $\text{Nb}(\eta^7\text{-C}_7\text{H}_7)(\eta^4\text{-C}_7\text{H}_8)(\text{PMe}_3)$ (**21**), or $\text{Nb}(\eta^7\text{-C}_7\text{H}_7)(\text{CO})_3$ (**22**) in moderate yields (Scheme 11).³⁵ These complexes are good precursors to other $\text{Nb}(\eta^7\text{-C}_7\text{H}_7)$ derivatives. Thus these one-pot reactions provide convenient routes to the virtually unexplored $\text{Nb}(\eta^7\text{-C}_7\text{H}_7)$ system.

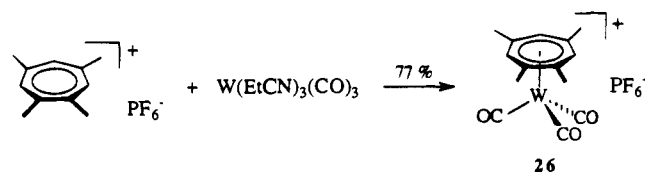
The sandwich complexes $\text{M}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_5\text{H}_4\text{R})$ ($M = \text{V, Nb, or Ta}$; $R = \text{H or Me}$) can be prepared by treating the corresponding η -(cyclopentadienyl)metal chlorides with magnesium or isopropylmagnesium bromide in the presence of cycloheptatriene.^{36–38} For example, the first η^7 -(cycloheptatrienyl)tantalum compound, namely $\text{Ta}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_5\text{H}_4\text{Me})$ (**23**) has been synthesized from $\text{Ta}(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Cl}_4$ (**24**) in 12% yield (Scheme 12).³⁷

Fischer *et al.* first reported the reduction of CrCl_2 , MoCl_5 , and WCl_6 in the presence of cycloheptatriene and cyclopentadiene (or cyclopentadienide). These reactions gave the mixed-sandwich compounds $\text{M}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_5\text{H}_5)$ ($M = \text{Cr, Mo, or W}$) in one-step but in very low yields (<2%).³⁹ An improved route to the molybdenum compound $\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_5\text{H}_5)$ (15% yield) was then reported which employs $\text{MoCl}_3(\text{THF})_3$ as starting material.³¹ Recently, the sandwich compounds $\text{M}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_5\text{H}_4\text{R})$ ($M = \text{Mo or W}$; $R = \text{H or Me}$) have been synthesized by reducing the corresponding η -cyclopentadienyl complexes $\text{M}(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Cl}_4$ with magnesium turnings or sodium amalgam in the presence of cycloheptatriene. These preparations, however, also suffer from a poor yield.⁴⁰

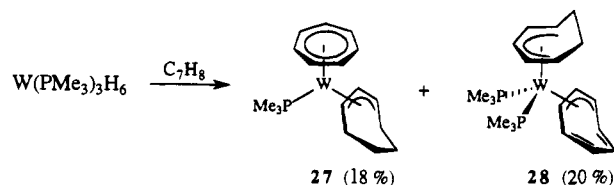
Scheme 13



Scheme 14



Scheme 15



$\text{C}_5\text{H}_4\text{R})\text{Cl}_4$ with magnesium turnings or sodium amalgam in the presence of cycloheptatriene. These preparations, however, also suffer from a poor yield.⁴⁰

Treatment of MoCl_5 with 5 equiv of sodium amalgam in the presence of excess cycloheptatriene affords a mixture of $\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_7\text{H}_9)$ (**5**) and $\text{Mo}(\eta^6\text{-C}_7\text{H}_8)_2$ (**6**) in 1:1.7 ratio. Upon mild thermolysis, compound **5** can be isolated as the sole product in 39% yield.⁴¹ Using $\text{MoCl}_4(\text{THF})_2$ as starting material gives similar results. The tungsten compound $\text{W}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_7\text{H}_9)$ (**25**) can also be prepared similarly from WCl_6 (Scheme 13).⁴² However, in contrast to the corresponding molybdenum chemistry, the bis-(cycloheptatriene) complex $\text{W}(\eta^6\text{-C}_7\text{H}_8)_2$ could not be isolated. Presumably the intramolecular hydrogen migration for $\text{W}(\eta^6\text{-C}_7\text{H}_8)_2$ is faster than that for **6**. The primary advantage of this method is the convenient preparation of synthetically useful compounds **5** and **25** in one pot and in gram quantities.

D. Other Methods

Nucleophilic attack on the C_7 ring in (η^7 -cycloheptatrienyl)metal complexes provides an alternative entry to (η^6 -cycloheptatriene)metal complexes. The details are illustrated in section VI.B.2.

In general, the reactions of tropylium cation with substitution-labile metal species do not give cycloheptatrienylmetal complexes. For example, treatment of $[\text{C}_7\text{H}_7][\text{BF}_4]$ with anion $[\text{Mn}(\text{CO})_5]^-$ only yields the self-coupled products $\text{Mn}_2(\text{CO})_{10}$ and $\text{C}_{14}\text{H}_{14}$.⁵ Nevertheless, this method has been utilized to prepare the (1,2,4,6-tetramethylcycloheptatrienyl)tungsten complex **26** (Scheme 14).⁴³

The readily available tungsten polyhydride complex $\text{W}(\text{PMe}_3)_3\text{H}_6$ can also be used to prepare cycloheptatrienyltungsten complexes. It reacts with cycloheptatriene at 80 °C giving a mixture of separable $\text{W}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_7\text{H}_{11})(\text{PMe}_3)$ (**27**) and $\text{W}(\eta^6\text{-C}_7\text{H}_8)_2(\eta^5\text{-C}_7\text{H}_9)(\text{PMe}_3)_2$ (**28**) (Scheme 15).⁴⁴

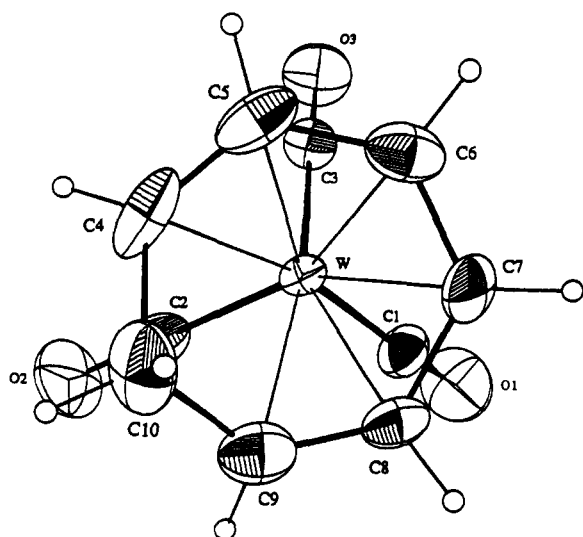
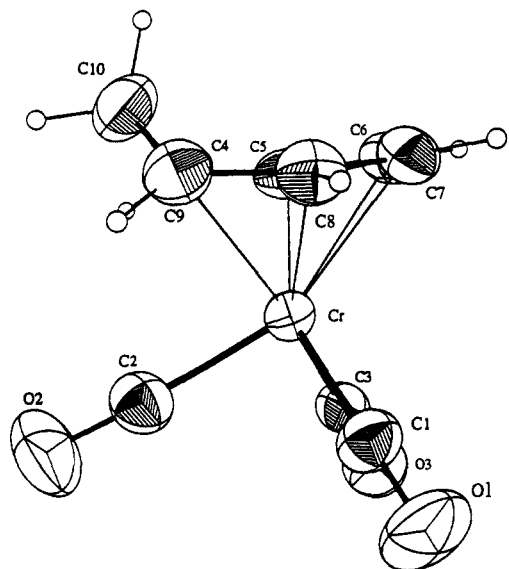


Figure 1. ORTEP drawings of (a) $\text{Cr}(\eta^6\text{-C}_7\text{H}_8)(\text{CO})_3$ and (b) $\text{W}(\eta^6\text{-C}_7\text{H}_8)(\text{CO})_3$.

IV. Structure

The structure of $\text{Mo}(\eta^6\text{-C}_7\text{H}_8)(\text{CO})_3$ was determined in 1960.⁴⁵ This showed that the triene ring carbon atoms are approximately coplanar with alternating single and double carbon-carbon bonds. The molecule adopts a staggered structure with an approximate symmetry plane which passes through the molybdenum atom, the unique carbonyl ligand, and the methylene group. Detailed analysis of the structures of chromium and tungsten analogs has recently been performed.⁴⁶ These compounds are entirely isostructural with the molybdenum compound. However, some points mentioned in the early study appear to oversimplify the actual situation. Figure 1 shows the ORTEP drawings of $\text{Cr}(\eta^6\text{-C}_7\text{H}_8)(\text{CO})_3$ and $\text{W}(\eta^6\text{-C}_7\text{H}_8)(\text{CO})_3$ in different perspective views. Close examination of the chromium (and tungsten) data reveals that atoms C4/C5/C8/C9 are planar within 0.002 Å (for W, 0.01 Å), while C6 and C7 lie 0.17 Å (for W, 0.14 Å) and 0.18 Å (for W, 0.16 Å) above the plane. The obtuse angle between the C4/C5/C8/C9 and C5/C6/C7/C8 planes is 171.0° (for W,

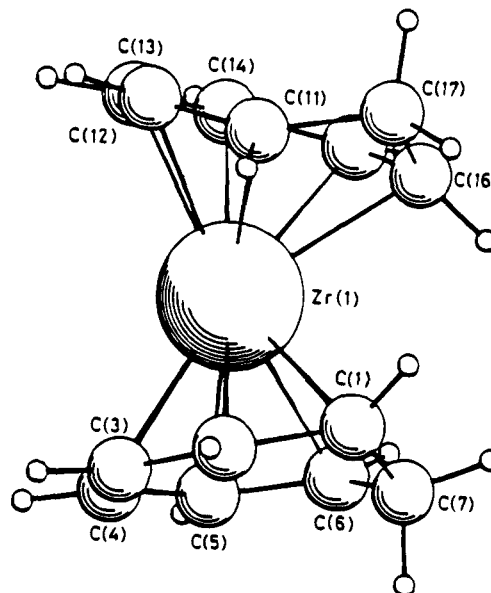


Figure 2. Molecular structure of $\text{Zr}(\eta^6\text{-C}_7\text{H}_8)_2$.

172.4°). Thus the coordinated cycloheptatriene ring actually exists in a flattened boat conformation.

Close inspection of the data for $\text{M}(\eta^6\text{-C}_7\text{H}_8)(\text{CO})_3$ ($\text{M} = \text{Cr}, \text{Mo}, \text{or W}$) also reveals that the six-membered pseudo-ring carbon-carbon bonds exhibit three different sets of values rather than two. For the Cr, Mo, and W compounds, the C4-C5 and C8-C9 bonds average 1.351 (15, 16, 6) Å, which is identical to the double-bond length in free cycloheptatriene while C5-C6 and C7-C8 bonds average 1.426 (17, 18, 6) Å, which is slightly longer than the single-bond length in free cycloheptatriene. The unusual observation is the lengthening of the C6-C7 bond, which averages 1.397 (15, 21, 3) Å. This distance is longer than the corresponding value for free cycloheptatriene and approaches the single-bond length observed in the pseudo-ring.

The other interesting observation for these structures is that the metals do not lie perpendicularly under the centroid, but shift slightly toward the C6-C7 π -bond in the pseudo-ring. This, together with the flattened boat conformation, argues that the ring may be described as η^4, η^2 -bound rather than η^6 -bound, with the C6-C7 bond acting independently of the C4-C5 and C8-C9 bonds.⁴⁶

The barriers of rotation about the cycloheptatriene-Cr axis of $\text{Cr}(\eta^6\text{-C}_7\text{H}_7\text{R})(\text{CO})_3$ ($\text{R} = \text{H}, \text{Me}, \text{OMe}, \text{Bu}^t, \text{or CN}$) have been determined by a complete lineshape analysis of the ¹³C resonances of the carbonyl groups as a function of temperature.⁴⁷ The values of ΔH^\ddagger depend slightly on the substituent at the 7-position and range from 37.2 to 45.6 kJ/mol.

The structure of $\text{Zr}(\eta^6\text{-C}_7\text{H}_8)_2$ (**16**) has recently been determined.²⁴ It shows an unusual bent arrangement with a dihedral angle between the best planes of the two C_7H_8 rings of 25.6° and the methylene groups are staggered and on the same side of the molecule (Figure 2). This is in contrast to that of $\text{Mo}(\eta^6\text{-C}_7\text{H}_8)_2$ (**6**), which has a normal parallel arrangement of the rings with the methylene groups on opposite side of the molecule.^{21b} The five C-C distances within the coordinated portion of the C_7 ring of **16** do not show alternating short and long

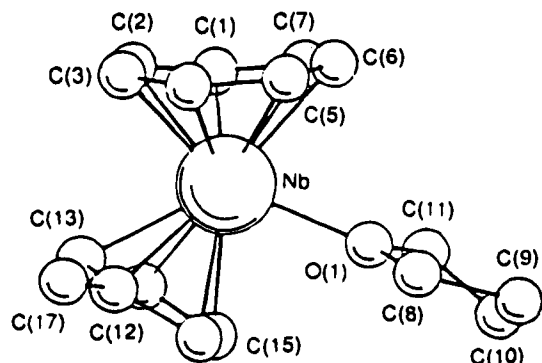


Figure 3. Molecular structure of $[\text{Nb}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_5\text{H}_4\text{-Me})(\text{THF})]^+$.

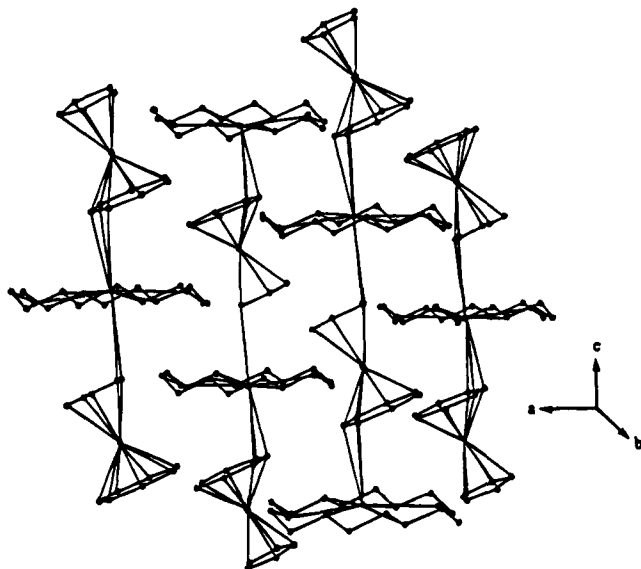


Figure 4. Crystal structure of $[\text{K}(18\text{-crown-6})][\text{Nb}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_5\text{H}_5)]$.

distances. Lack of alternation has also been found for $\text{Nb}(\eta^6\text{-C}_7\text{H}_8)(\text{PMe}_3)_2\text{Cl}_2$ ^{35b} and $\text{Zr}(\eta^6\text{-C}_7\text{H}_7\text{SiMe}_3\text{-7})(\text{PMe}_3)_2\text{I}_2$.²⁷

The structures of $(\eta^7\text{-cycloheptatrienyl})$ metal complexes usually show a planar and regular seven-membered ring bound symmetrically to the metal center. For example, the molecular structure of $\text{Nb}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_5\text{H}_5)$ in the gas phase, which has recently been determined by electron diffraction at 470 K, shows that the niobium atom is sandwiched by two parallel and symmetric rings.^{48a} However, some exceptions have been reported. For example, the cycloheptatrienyl ring in $[\text{Nb}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_5\text{H}_4\text{Me})(\text{THF})][\text{PF}_6]$ is not planar, but displays a significant "dishing" of the ring as defined by the Nb–C bond lengths (Figure 3).^{37,48b} The salt $[\text{K}(18\text{-crown-6})][\text{Nb}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_5\text{H}_5)]$ has an unusual crystal structure. As shown in Figure 4, the potassium ion is not equidistant from each of the carbons of a particular ring. As a result, there is a marked variation of C–C bond lengths within the C₇ ring.^{37,48b}

Deviation of the C₇ ring substituents from the plane defined by the ring carbon atoms has been observed for some $(\eta^7\text{-cycloheptatrienyl})$ metal complexes. For example, the average bending of the C₇ hydrogen atoms is 10° toward the Ti atom in $\text{Ti}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_5\text{Me}_5)$ (Figure 5).³³ The hydrogen atoms of the $\eta^7\text{-C}_7\text{H}_7$ group in $[\text{Ti}(\eta^7\text{-C}_7\text{H}_7)(\text{THF})(\mu\text{-Cl})_2]$ (11) and

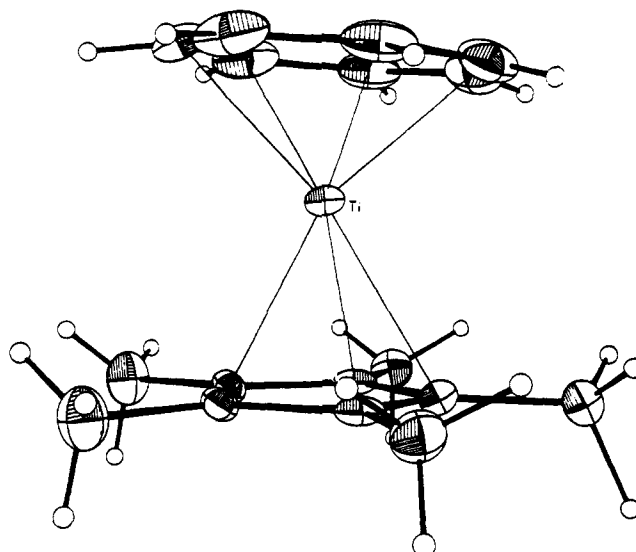


Figure 5. Molecular structure of $\text{Ti}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_5\text{Me}_5)$.

$\text{Ti}(\eta^7\text{-C}_7\text{H}_7)(\text{dmpe})\text{Et}$ also have a similar out-of-plane displacement.²² Such deviation can be attributed to a reorientation of the ring for better metal overlap.⁴⁹ It is worth mentioning that the zirconium analog $\text{Zr}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_5\text{Me}_5)$ does not show a similar bending.⁵⁰ Presumably, the larger Zr fits better than Ti and no inward bending and consequent rehybridization is necessary.

The activation energies for ring rotation in solid $[\text{M}(\eta^7\text{-C}_7\text{H}_7)(\text{CO})_3][\text{BF}_4]$ ($\text{M} = \text{Cr}$ or Mo) have been determined by proton spin–lattice relaxation time measurements.⁵¹ These values are quite close (Cr , 12.8; Mo , 13.6 kJ/mol) which may reflect the fact that these complexes are isostructural with similar packing densities.

V. Bonding

The $\eta^6\text{-cycloheptatriene}$ ligand can be considered as a coordinated triene and the bonding scheme for $\text{M}(\eta^6\text{-C}_7\text{H}_8)$ is well-documented.⁵² Recently, an examination of the bonding in $\text{Zr}(\eta^6\text{-C}_7\text{H}_8)_2$ (16) and its variation with the angle between the rings has been performed using charge-iterative extended Hückel molecular orbital calculations.^{24b} The MO diagram of 16 obtained from the calculations is shown in Figure 6, which also illustrates how the frontier MO's can be derived from those of benzene. It is evident that on opening the ring linkage between C(1) and C(6) those orbitals which are bonding across C(1) and C(6) are destabilized and those which are antibonding between C(1) and C(6) are stabilized. These shifts result in the HOMO π_3 being higher in energy in cycloheptatriene than in benzene and the LUMO π_4 being lower in energy in cycloheptatriene than in benzene. Cycloheptatriene is thus set up to be both a better donor and a better acceptor than benzene. Orbital 43, the LUMO in 16, is essentially a d_{z^2} orbital, whereas orbitals 44 and 45 are hybrid orbitals in which the $d_{x^2-y^2}$ and d_{xy} orbitals mix strongly with the two π_4 orbitals from the rings.

Studies of the effects of bending the cycloheptatriene rings have showed that orbitals 44 and 45 exhibit a stabilization in energy on bending with a minimum energy at a similar angle to that obtained

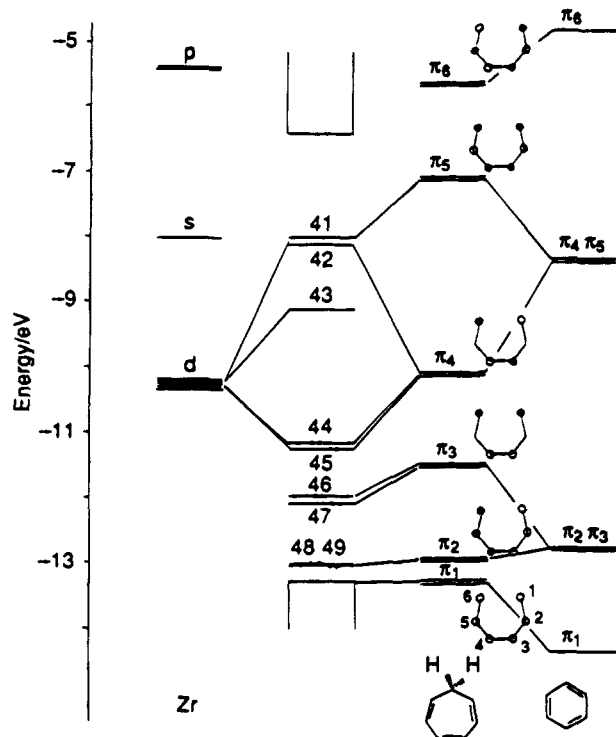


Figure 6. Qualitative molecular orbital diagram for $\text{Zr}(\eta^6\text{-C}_7\text{H}_8)_2$.

Scheme 16



from the X-ray structure, although they predict a slight destabilization in the total energy for the system. Similar stabilization has not been obtained for other orbitals in **16**.^{24b}

The origin of the staggered structure in **16** has also been discussed.^{24b} For an eclipsed configuration of the complex (C_{2v} symmetry), combinations of π_4 transform as b_2 and a_2 , but $d_{x^2-y^2}$ and d_{xy} transform as b_2 and a_1 , so only one of the d orbitals is of correct symmetry to back-donate to the ligand. If, however, the complex is staggered (C_2 symmetry) then both orbitals can back-donate as shown in Scheme 16. The geometric structure of **16** has also been predicted by ab initio MO calculations to yield a consistent interpretation of the experimental data.⁵³

The bonding between the metal and η^7 -cycloheptatrienyl ligand, however, has been the subject of recent debate. This ligand was originally regarded as a coordinated aromatic tropylium ion $\eta^7\text{-C}_7\text{H}_7^+$ and thus classified as a 6-electron donor. However, recent studies have shown that the assignment of +1 formal charge to this ligand in its complexes is inappropriate. For example, it gives the misleading impression that the $\eta^7\text{-C}_7\text{H}_7$ ligand is more susceptible to nucleophilic attack than other coordinated polyenes; in fact, according to the Davies, Green, and Mingos rules,⁵⁴ it is the least susceptible to nucleophilic attack of all common coordinated polyenes. Moreover, X-ray photoelectron spectroscopy studies on

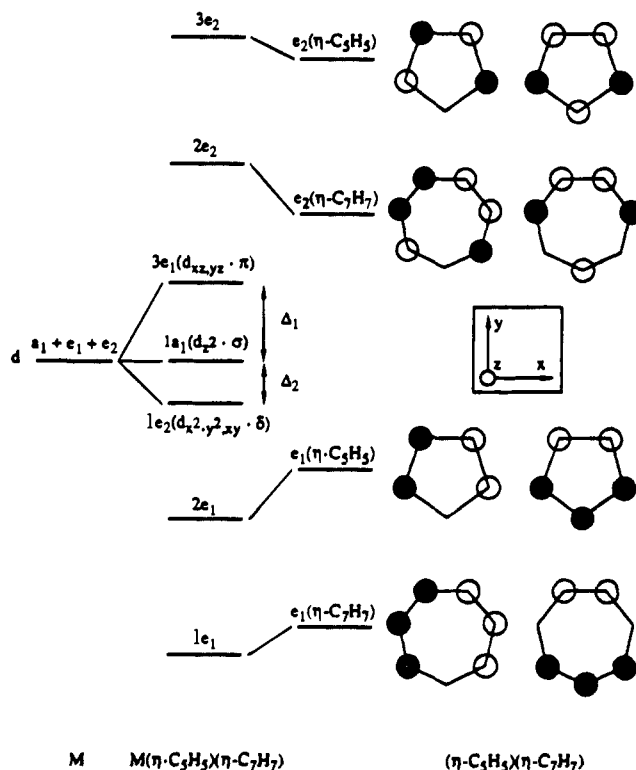


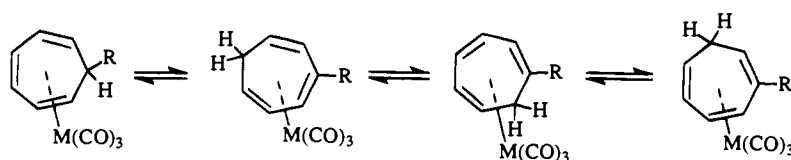
Figure 7. Qualitative molecular orbital diagram for $\text{M}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_5\text{H}_5)$.

$\text{M}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_5\text{H}_5)$ ($\text{M} = \text{Cr}, \text{V}, \text{or Ti}$) have showed that the oxidation state of the metal increases in the sequence $\text{Cr} < \text{V} < \text{Ti}$. In the Ti compound, there is greater localization of the negative charge on the C_7 ring (0.7–0.8 electrons) than on the C_5 ring (0.3–0.4 electrons).⁵⁵ Similar results have also been obtained from ab initio calculation,⁵⁶ metalation experiments,⁵⁷ and ^{13}C NMR studies on this type of compounds.⁵⁸

In an extensive study of $\text{Ti}(\eta^7\text{-C}_7\text{H}_7)$ chemistry,²² Green *et al.* have found that the $\text{Ti}(\eta^7\text{-C}_7\text{H}_7)$ moiety is markedly reluctant to form any 18-electron complexes and it prefers to form 16-electron complexes $\text{Ti}(\eta^7\text{-C}_7\text{H}_7)\text{L}_2\text{X}$ where L is a 2-electron donor ligand and X is a 1-electron σ -bonded group. This observation is also not consistent with the common formulation of the cycloheptatrienyl group as C_7H_7^+ . Since if the $\eta^7\text{-C}_7\text{H}_7$ group is given a formal charge of +1, the $[\text{Ti}(\eta^7\text{-C}_7\text{H}_7)]^+$ group might be expected, by analogy with $\text{V}(\eta^5\text{-C}_5\text{H}_5)$ which is also by definition d^4 , to form 18-electron complexes such as $[\text{Ti}(\eta^7\text{-C}_7\text{H}_7)(\text{CO})_4]^+$ [cf. $\text{V}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_4$]. However, no complexes with π -acceptor ligands have been isolated.

In order to study the nature of the $\text{M}(\eta^7\text{-C}_7\text{H}_7)$ bond, Green *et al.* have performed photoelectron (PE) spectroscopic studies on the sandwich compounds $\text{M}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_5\text{H}_5)$ ($\text{M} = \text{Ti}, \text{V}, \text{Nb}, \text{Cr}, \text{or Mo}$) and $\text{Ta}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_5\text{H}_4\text{Me})$.^{22b,37,59,60} Sandwich compounds have been chosen because they give rise to PE spectra with well-separated bands of metal, ligand, and mixed-metal/ligand character. A qualitative MO diagram for these sandwich compounds is shown in Figure 7 in which only the e symmetry π orbitals of the ligands are considered.³⁷ The metal d orbitals split into three sets; d_{z^2} ($1a_1$), d_{xz} , d_{yz} ($3e_1$) and $d_{x^2-y^2}$, d_{xy} ($1e_2$), which are of σ , π , and δ symmetry respectively with respect to the metal-ring axes. The

Scheme 17



$1a_1$ orbital is essentially non bonding. The $3e_1$ orbitals are strongly antibonding and the $1e_2$ orbitals are metal \rightarrow carbon back-bonding in nature. Since the e_1 and e_2 orbitals of C_7 ring are lower than those of C_5 ring, the e_2 interaction will take place primarily via C_7 ring while the e_1 involvement remains predominantly with C_5 ring. Thus the localization of $1e_2$ MO's is of central importance in determining the nature of the $M-(\eta^7-C_7H_7)$ bond. If these orbitals are largely metal-localized, this implies that the metal \rightarrow carbon back-bonding is relatively weak, whereas if there is a significant contribution from the ligand, the metal-ligand δ interaction is strong.

It has been shown by the PE data that for $Ti(\eta^7-C_7H_7)(\eta^5-C_5H_5)$, the four least tightly bound electrons in $1e_2$ MO's are substantially localized on the C_7 ring, and have the primary role in forming the covalent bonds between the ring and the metal.^{22b,59} Formally three of these electrons are derived from the metal and thus the compound is considered to have a Ti(IV) (d^0) metal center. Consequently, this description redefines the formal charge of the ligand $\eta^7-C_7H_7$ as -3 . In which case the Hückel $4n + 2$ rule for aromaticity is still satisfied. The proposal is in accord with the general pattern of $Ti(\eta^7-C_7H_7)$ chemistry. The harder bases, such as ethers and amines, are more tightly bound to $[Ti(\eta^7-C_7H_7)]^+$ moiety than the softer bases, such as phosphines, indicating that the metal center is more d^0 than d^4 in character.

In contrast, by comparing the relative intensities of the photoelectron bands in the He I and He II spectra of group 5 sandwich compounds, it has been shown that the $1e_2$ level contains a significant contribution from both ligand and metal valence atomic orbitals.^{37,59}

In a systematic PE spectroscopic study of $[M(\eta^m-C_mH_m)(\eta^n-C_nH_n)]$ ($m, n = 5, 6, 7, \text{ or } 8$), it has been found that the ring contribution in the e_2 MO's increases with ring size and decreases with increase in the metal atomic number across the transition series.^{59,61} The results are consistent with the observation that the negative charge on the C_7 ring in $M(\eta^7-C_7H_7)(\eta^5-C_5H_5)$ ($M = Cr, V, \text{ or } Ti$) follows the order: $Ti > V > Cr$.⁵⁵ Although the ligand contribution in the $1e_2$ MO's is smaller in $Cr(\eta^7-C_7H_7)(\eta^5-C_5H_5)$ than in the Ti and V analogs, it has been noted that the a_1-e_2 splitting in $Cr(\eta^7-C_7H_7)(\eta^5-C_5H_5)$ (1.6 eV) is substantially greater than that in $Cr(\eta^6-C_6H_6)_2$ (0.9 eV), suggesting the high contribution the C_7 ring e_2 orbitals makes to the e_2 MO's.⁵⁹

The relative metal and ligand contributions to the $1e_2$ MO's in these sandwich compounds has recently been estimated as around 60–80% metal character by using synchrotron radiation to provide access to a wide range of incident photon energies.⁶⁰ This indicates that neither the $+1$ nor -3 formalism for the charge on the cycloheptatrienyl ring is an accurate description of the metal-ring bonding in these

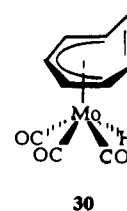
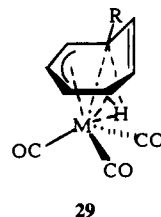
complexes. Accordingly, it has been proposed that the η^7 -cycloheptatrienyl ligand is best described as a 7-electron donor and a trivalent ligand and that three metal electrons are required to form the $M-(\eta^7-C_7H_7)$ covalent bond.

VI. Reactivity

A. Cycloheptatriene Metal Complexes

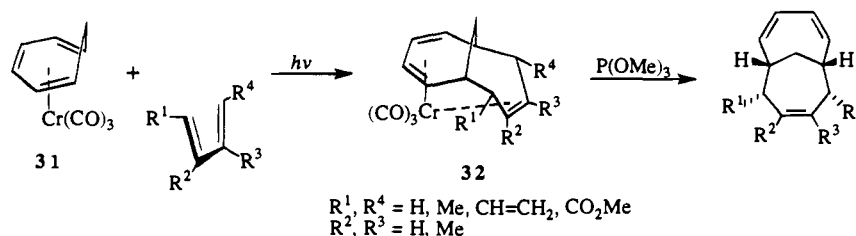
1. Sigmatropic Rearrangements

By using the deuterium-labeled cycloheptatriene-molybdenum complex $Mo(\eta^6-C_7H_7D-7)(CO)_3$, Roth and Grimme showed that the 7-*endo*-hydrogen migrates leading to an essentially complete deuterium scrambling. It was suggested that the process might involve initial migration of the hydrogen to the metal with formation of the cycloheptatrienyl molybdenum hydride species $Mo(\eta^7-C_7H_6D)(CO)_3H$.⁶² The related processes for $Cr(\eta^6-C_7H_7R-7)(CO)_3$ ($R = Me, Ph, \text{ or } p\text{-tolyl}$) was studied by Pauson *et al.* who confirmed that only the *exo*-isomers are capable of such rearrangement. However, the stepwise formation of the substituted derivatives and the stereospecificity of the rearrangement suggested that the overall process involves a series of sequential 1,5-hydrogen migrations (Scheme 17) and the transition state **29**.⁶³ This was further supported by the work by Brown *et al.* They prepared a tricarbonylmolybdenum complex with ^{13}C -labeled cycloheptatriene and then followed the thermolysis of this compound by ^{13}C NMR. The redistribution of isotopic label in the product was compared with that predicted from solving the differential equations describing the kinetics of each of the possible rearrangement pathways.⁶⁴ It was thus confirmed that a 1,5-hydrogen shift is involved. Low-temperature matrix isolation studies showed that thermal rearrangement of $Mo(\eta^6-C_7H_8)(CO)_3$ in the gas phase produces a new species which have $\nu(CO)$ at 1909, 1957, and 2042 cm^{-1} . It was proposed to be the metal hydride complex $Mo(\eta^5-C_7H_7)(CO)_3H$ (**30**).⁶⁵

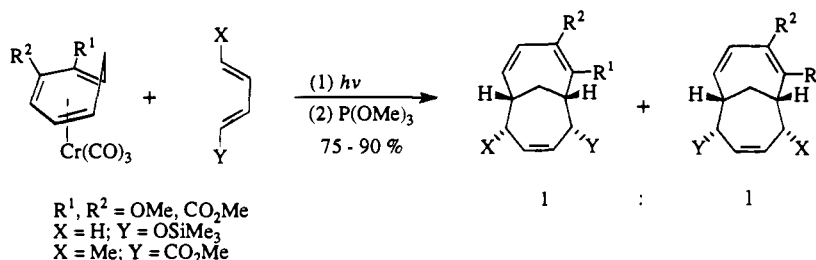


As mentioned in section III.A, the reaction of $Mo(CO)_6$ with 1,3,5,7-tetramethylcycloheptatriene gives a mixture of **1**, **2**, and **3** in 53, 21, and 8% yield, respectively (Scheme 2).¹² The formation of **2** and **3** may be ascribed to a series of sequential 1,5-hydrogen

Scheme 18



Scheme 19



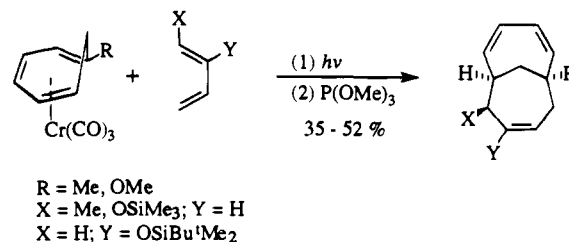
migrations in the initially formed **1**. This has been verified by heating a solution of pure **1** under similar conditions. The ^1H NMR spectrum of the resulting solution shows that it contains compounds **1**, **2**, and **3** in 6:2.5:1 ratio, which is close to that found in the initial reaction. It was suggested by Pauson *et al.* that substituents in the 1-position might hinder the formation of the proposed transition state **29**.^{63b} Thus compounds having 1- and 6-substitution do not undergo further rearrangement as in the case of compounds **2** and **3**.

2. Cycloaddition Reactions

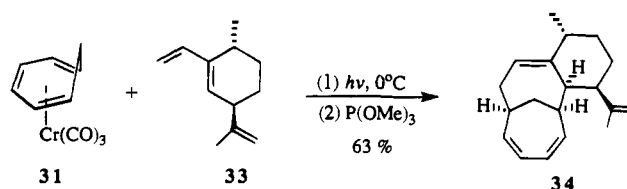
Higher order cycloaddition reactions ($6\pi + 4\pi$, $6\pi + 2\pi$, $4\pi + 4\pi$) usually proceed with a high level of stereoselectivity. However, the chemical yields of these reactions are relatively low due to the small periselectivity. For example, the thermal reactions of cycloheptatriene with dienes give a myriad of products of which the $[6 + 4]$ adduct is only a minor component.⁶⁶ Kreiter *et al.* demonstrated that the cycloaddition reaction can be promoted by a transition metal.⁶⁷ The photochemical reactions of $\text{Cr}(\eta^6\text{-C}_7\text{H}_8)(\text{CO})_3$ (**31**) with 1,3-butadiene and its derivatives give the bicyclo[4.4.1]undecane adducts **32** in good yields which can be demetallated by the action of $\text{P}(\text{OMe})_3$ (Scheme 18).⁶⁸ These transition metal-mediated cycloadditions have been further elaborated by Rigby *et al.*⁶⁹ They have studied the regio- and stereoselectivity of these reactions by employing substituted derivatives of **31** and a range of substituted butadienes. Both electron-rich and electron-deficient dienes participate equally well in the transformation giving only the *endo* diastereomer. For 2- and 3-substituted cycloheptatriene complexes, the reactions show little regioselectivity which is exemplified in Scheme 19. However, for 1-substituted cycloheptatriene complexes, the reactions display high regioselectivity in some cases which are presumably due to steric factors (Scheme 20).⁷⁰

Diastereoselectivity has been observed for the photocycloaddition of **31** with optically pure dienes.^{70,71}

Scheme 20



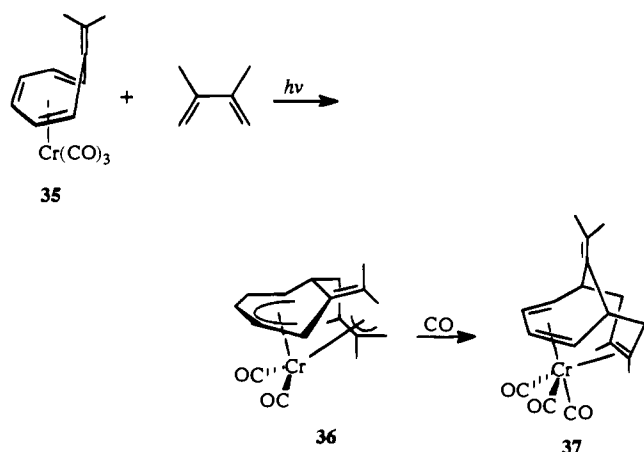
Scheme 21



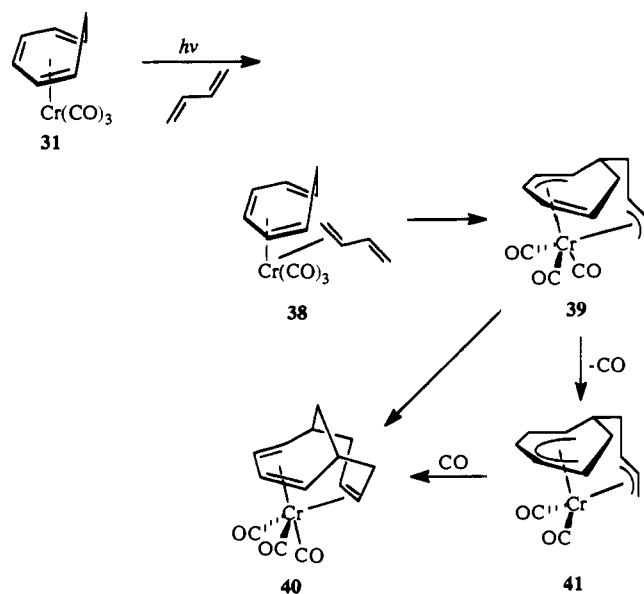
A promising example has been reported which involves the cycloaddition of **31** with diene **33**. The reaction gives **34** in 63% yield and less than 5% of its diastereomer could be detected (Scheme 21).⁷¹

It is worth noting that the photochemical reaction of heptafulvene complex **35** with 2,3-dimethyl-1,3-butadiene gives the unexpected product **36** in good yield. Treatment of **36** with CO (1 atm) at 0 °C results in the formation of the usual adduct **37** (Scheme 22).⁷² This observation suggests that the chromium-mediated $[6 + 4]$ cycloaddition is not a concerted reaction but a stepwise process. A plausible mechanism has been proposed which is illustrated in Scheme 23.^{67,72b} The first step is a light-induced η^6 to η^4 hapticity change of the triene ligand, leaving a vacant site to which the diene is coordinated. Then a C–C coupling occurs between the diene and the C(1) atom in the cycloheptatriene giving the complex **39**. A further C–C coupling gives the cycloadduct **40**, while loss of a CO produces the η^3, η^5 -complex **41**. The mechanism has been reexamined by Stufkens *et al.*, who study the primary photoprocesses in low-temperature matrices and the

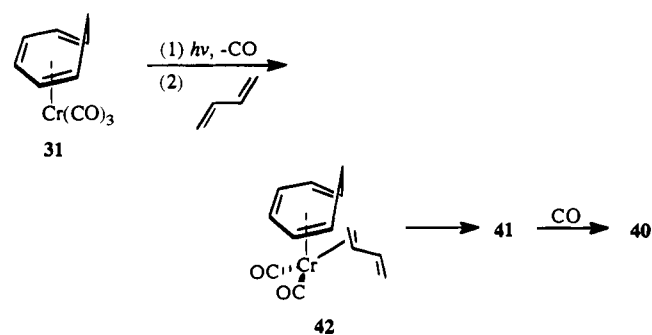
Scheme 22



Scheme 23



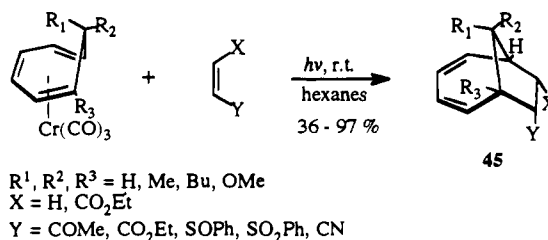
Scheme 24



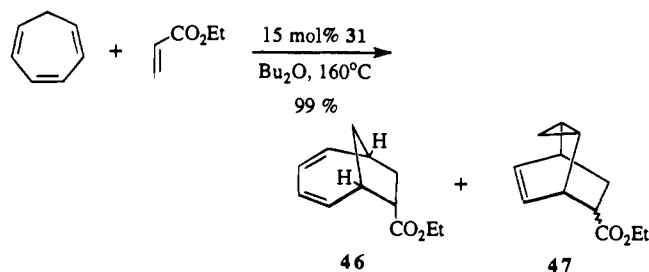
secondary thermal reactions in liquefied noble gases with infrared spectroscopy.⁷³ Although both CO loss and η^6 to η^4 hapticity change of the triene ligand have been observed, in solution, only the CO loss gives rise to the coupling reaction. Accordingly, an alternative mechanism has been proposed (Scheme 24). Light-induced ejection of CO produces the coordinatively unsaturated complex $\text{Cr}(\eta^6\text{-C}_7\text{H}_8)(\text{CO})_2$, which binds to the diene forming **42**. A C–C coupling followed by recapture of the dissociated CO leads to the adduct **40**.

The molybdenum and tungsten congeners $\text{M}(\eta^6\text{-C}_7\text{H}_8)(\text{CO})_3$ [M = Mo (**43**) or W (**44**)] have also been

Scheme 25



Scheme 26

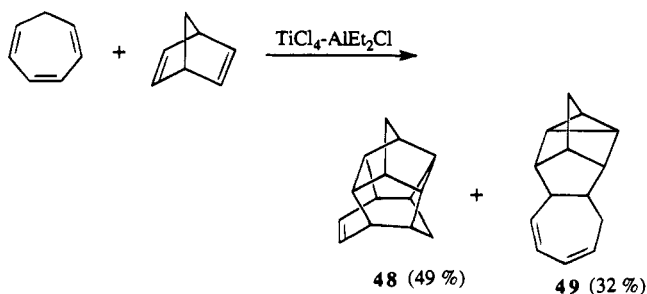


examined as substrates in the photoinduced [6 + 4] cycloaddition reaction.⁷⁰ The molybdenum complex **43** also promotes the cycloadditions but the chemical yields are uniformly lower than those for the chromium reactions. This has been rationalized by the weaker bond strength of Mo–C₇H₈ bond. Presumably, the complex strips of the metal center readily and thus does not effectively participate in the cycloaddition process. The tungsten analog **44** is totally ineffective for promoting the cycloadditions which may due to the fact that **44** has the strongest metal–ligand bonding in the group 6 series.⁷⁴

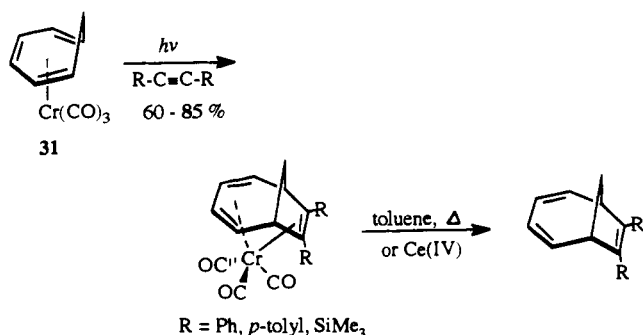
The related photoinduced [6 + 2] cycloaddition has also been reported.^{75,76} Irradiation of a mixture of **31** or its derivatives and electron-deficient alkenes in hexanes at room temperature gives the metal-free bicyclo[4.2.1]nonadiene adducts **45** in good yields (Scheme 25). The reactions afford a single diastereomer resulting from an *endo* approach of the trienophile. It is noted that reactions with electron-rich alkenes do not give the desired adducts. This may be related to the strength of metal–alkene bond in the intermediate analogous to **42** that is presumably involved in these transformations. The electron-donating groups on the 2π partner diminish the $d\text{-}\pi^*$ back-bonding, thus weaken the metal–alkene bond.

These [6 + 4] and [6 + 2] cycloadditions can also be effected by thermal activation. Heating complex **31** with dienes or alkenes in refluxing di-*n*-butyl ether affords high yields of the corresponding metal-free adducts directly.^{70,76,77} The products obtained by this means are identical in every respect to those obtained in the photochemical reactions. Interestingly, the same transformations can also be achieved by using a catalytic amount of a transition metal complex. For example, heating cycloheptatriene with excess ethyl acrylate in the presence of 15 mol % of **31** gives a mixture of **46** and **47** in 10:1 ratio and 99% yield (Scheme 26). Using smaller amounts of **31** (2 mol %) results in enhanced discrimination in the formation of **46** and **47** (98:2) but in a lower yield (55%).^{76,77} The reaction of cycloheptatriene with an excess of 1-acetoxy-1,3-butadiene in the presence of

Scheme 27



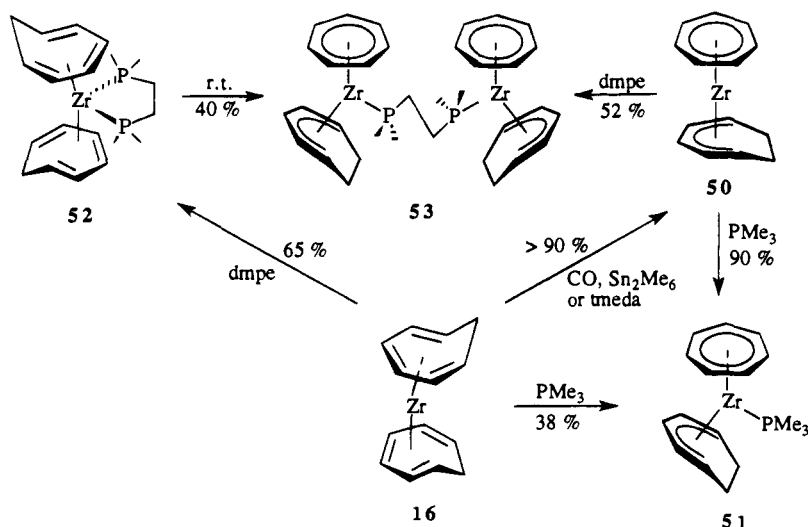
Scheme 28



ca. 30 mol % $\text{Cr}(\eta^6\text{-C}_7\text{H}_8)(\text{PPh}_3)(\text{CO})_2$ generates the expected adduct in 36% yield.⁷⁰ The cycloaddition of cycloheptatriene with 1,3-butadiene and norbornadiene can also be catalyzed by the $\text{TiCl}_4\text{-AlEt}_2\text{Cl}$ system.^{78a} The former reaction gives the [6 + 2] and [6 + 4] adducts in 78 and 8% yield, respectively, while the latter reaction affords compound **48** and the [2 + 2 + 2] adduct **49** (Scheme 27). The formation of **48** is attributed to a [6 + 2] cycloaddition followed by an intramolecular Diels-Alder reaction.

The [6 + 2] cycloadditions can be extended to alkynes as trienophiles. Photolysis of **31** and alkynes results in the formation of the corresponding adducts which can be decomplexed with either toluene at elevated temperature or Ce(IV) ion (Scheme 28).^{79,80} The [6 + 2] cycloaddition of cycloheptatriene to phenyl(trimethylsilyl)acetylene can also be catalyzed by the catalytic system $\text{TiCl}_4\text{-AlEt}_2\text{Cl}$.^{78b}

Scheme 29



3. Lewis Base Addition Reactions

The 16-electron complex $\text{Zr}(\eta^6\text{-C}_7\text{H}_8)_2$ (**16**) is stable to hydrogen migration in the absence of Lewis base which is in contrast to the related titanium and molybdenum compounds. However, treatment of compound **16** with CO , Sn_2Me_6 , or tmeda produces compound $\text{Zr}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_7\text{H}_9)$ (**50**) in excellent yields. The reaction between **16** and PMe_3 behaves differently. It gives compound **51**, a thermally sensitive PMe_3 adduct of **50**. The related reaction of **16** with dmpe leads to the thermally unstable $\text{Zr}(\eta^4\text{-C}_7\text{H}_8)_2(\text{dmpe})$ (**52**), which is rapidly converted into the dimer **53** at room temperature. The compound **53** can also be directly prepared by treating compound **50** with dmpe (Scheme 29).²⁴

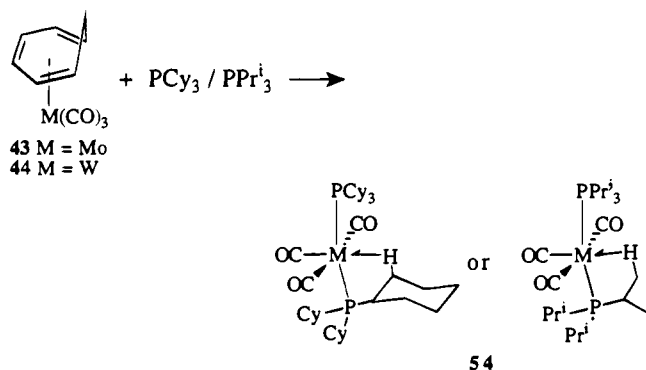
4. Ligand Exchange Reactions

The cycloheptatriene ring in $\text{M}(\eta^6\text{-C}_7\text{H}_8)(\text{CO})_3$ [$\text{M} = \text{Cr}$ (**31**), Mo (**43**), or W (**44**)] is relatively labile and can be displaced with a wide range of neutral ligands. The enthalpies of substitution of the complexes $\text{M}(\eta^6\text{-C}_6\text{H}_6)(\text{CO})_3$ ($\text{M} = \text{Cr}, \text{Mo}$, or W) with cycloheptatriene have recently been determined by solution calorimetry.⁸¹ The values ($-\Delta H$, kJ/mol) increase from Cr (27.2) to Mo (38.0) to W (53.1) showing that the $\text{M-C}_7\text{H}_8$ bond strength increases down the group. The ease of release of the cycloheptatriene ring in substitution reactions, however, was observed to decrease down the series $\text{Mo} > \text{W} > \text{Cr}$.⁸²

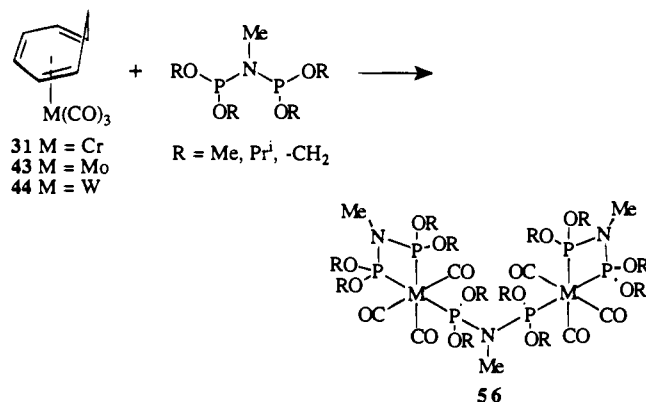
The reaction of **43** or **44** with the bulky phosphines PCy_3 or PPr^i_3 results in the formation of the formally five-coordinate, 16-electron complexes $\text{M}(\text{PR}_3)_2(\text{CO})_3$ (**54**) ($\text{M} = \text{Mo}$ or W ; $\text{R} = \text{Cy}$ or Pr^i) (Scheme 30).⁸³ The structures of the tungsten complexes have been determined which show the presence of agostic $\text{C-H}\cdots\text{M}$ interactions. It is worth mentioning that these molecules add dihydrogen to form stable $\eta^2\text{-H}_2$ complexes.⁸⁴ Thus, they represent rare examples in which both C-H and H-H bond activation occur at a single metal center.

Treatment of **31** with PR_3 ($\text{R} = \text{Cy}$ or Pr^i) does not lead to the chromium analog $\text{Cr}(\text{PR}_3)_2(\text{CO})_3$ (**55**). However, by employing $\text{Cr}(\eta^6\text{-naphthalene})(\text{CO})_3$ as the starting material, the reaction gives **55** ($\text{R} = \text{Cy}$)

Scheme 30



Scheme 31



in good yield.⁸⁵ Failure to produce **55** from **31** may be due to thermodynamic factors. Since the reactions of Cr(η^6 -naphthalene)(CO)₃ with various ligands are about 40 kJ/mol more exothermic than analogous reactions of **31**, this may provide the additional driving force necessary for forming **55**.

Compound Mo(η^6 -C₇H₈)(CO)₃ (**43**) reacts with tris-(2,4,6-trimethoxyphenyl)phosphine (TMPP) to give Mo(η^3 -TMPP)(CO)₃ of which the molecular structure shows an octahedral geometry with the TMPP ligand bound to the metal in tridentate mode with the phosphorus atom and two of the methoxy groups.^{86a}

Reaction of **31** with bidentate ligands Ph₂PCH₂CH₂-AsPh₂ (ape) and Ph₂AsCH₂CH₂AsPh₂ (dae) affords *mer*-Cr(CO)₃(η^1 -ape)(η^2 -ape) and *fac*-Cr(CO)₃(η^1 -dae)(η^2 -dae), respectively. The monodentate ape ligand in the former complex is coordinated through phosphorus as shown by ³¹P NMR studies.^{86b}

Displacement of C₇H₈ ligand in **31**, **43**, and **44** with other novel ligands has also been reported. For example, the reaction of these compounds with the ligands MeN[P(OR)₂]₂ (R = Me, Prⁱ, or -CH₂) leads to the ligand-bridged dimers **56** in *all-mer*, *all-fac*, and *mer-fac* forms depending on the ligand and conditions used (Scheme 31).⁸⁷ For M = W, the reactions also yield the novel cycloheptatriene-bridged dimers *mer*-{W(CO)₃{MeN[P(OR)₂]₂}}₂(μ - η^2 : η^2 -C₇H₈) (**57**) as minor products. The structure of **57** (R = Me) (Figure 8) confirms that the two metal fragments bond to the two nonadjacent carbon-carbon double bonds in the cycloheptatriene ring, which adopts a tub conformation with the metal moieties on the same face.⁸⁸

The reaction of **43** with the diphosphabenzene **58** leads to C₇H₈ substitution giving the complex **59**,

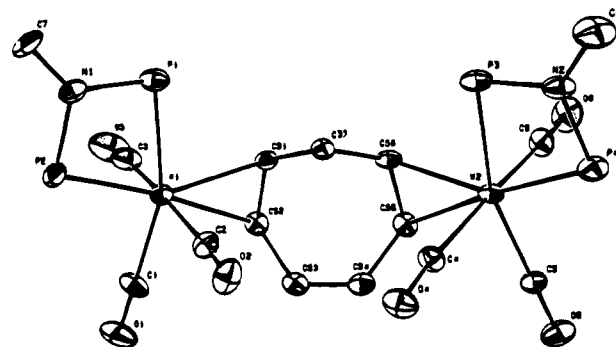
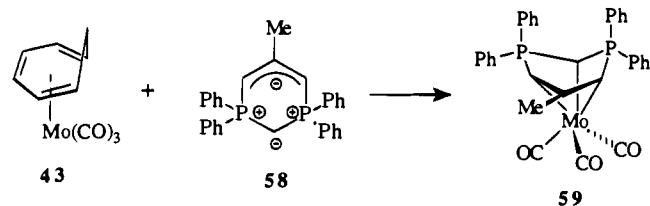


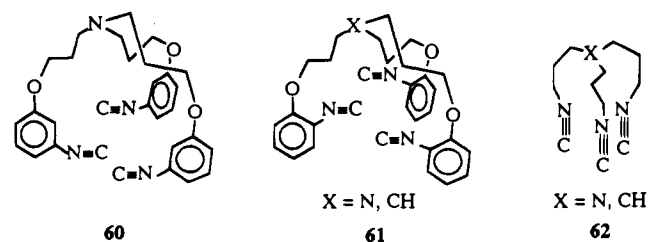
Figure 8. Molecular structure of *mer*-{W(CO)₃{MeN[P(OMe)₂]₂}}₂(μ - η^2 : η^2 -C₇H₈). Methoxy group omitted for clarity.

Scheme 32



which has been structurally characterized (Scheme 32).^{89a} The heterocycle **58** is coordinated to the metal via the methallylic π -system and via the semilydic carbon atom. The product **59** thus preserves a 18-electron configuration. Displacement of C₇H₈ ring from **43** by K₃E₇ (E = P, As, or Sb) has recently been reported.^{89b} The reactions give the trianions [Mo(CO)₃E₇]³⁻, which comprise distorted nornbornadiene-like η^4 -E₇³⁻ groups bound to Mo(CO)₃ center.

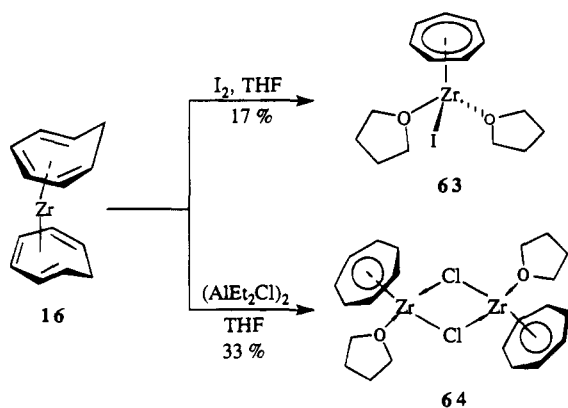
The tripodal triisocyanide ligands **60-62** can also displace the cycloheptatriene ring in **31**, **43**, and **44** to give the corresponding chelate complexes *fac*-M(CO)₃L.⁹⁰ Treatment of **43** with molar equivalence



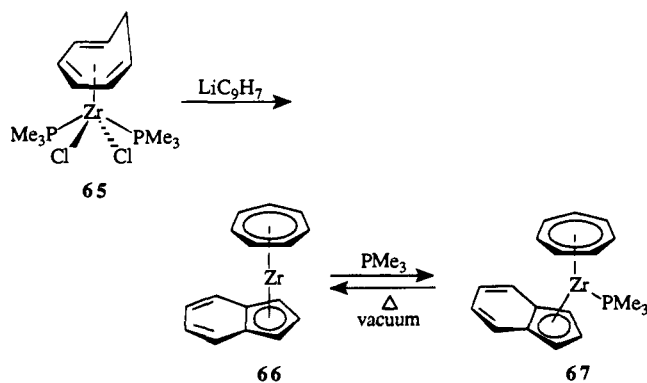
of PPh₃, Et₃N, and picolinic or quinaldinic acid also leads to ring displacement producing the salt [Et₃NH][Mo(CO)₃(PPh₃)L] (L = 2-picolate or 2-quinaldinate).⁹¹

Thermal substitution of the CO ligand in **31**, **43**, and **44** is rare and only one example was reported.⁹² In contrast, photoinduced CO substitutions for these complexes are well-documented. Irradiation of the chromium complex **31** in the presence of neutral ligands L, such as PPh₃, PMe₃, AsMe₃, P(OMe)₃, or P(OPh)₃ gives the complexes Cr(η^6 -C₇H₈)(CO)₂L.⁹³ The photochemistry of **31** and the molybdenum analog **43** in low-temperature gas matrices has been studied by Rest *et al.*^{94,95} Infrared spectroscopic studies show that UV irradiation of these compounds in CH₄ and Ar matrices at 12 K leads to ejection of CO to form the coordinatively unsaturated M(η^6 -C₇H₈)(CO)₂ in a reversible manner. Photolysis of **31**

Scheme 33



Scheme 34



or **43** in a N_2 matrix produces the dinitrogen complexes $M(\eta^6-C_7H_8)(CO)_2N_2$. In a CO matrix, stepwise photoelimination of cycloheptatriene occurs to give $M(CO)_6$ via the intermediate species $M(\eta^4-C_7H_8)(CO)_4$.

5. Redox Reactions

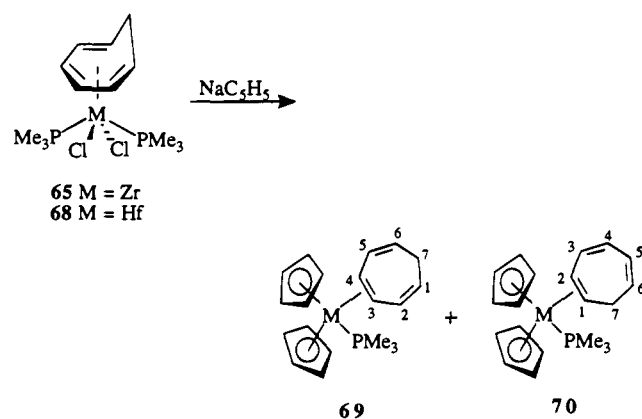
The electrochemistry of **31**, **43**, and **44** has been examined at a Pt electrode in aprotic solvents.⁹⁶ The study shows that this series of compounds have a different electrochemical behavior depending on the solvent. All of them are converted into $M(CO)_6$ via the cations $[M(\eta^6-C_7H_8)(CO)_3]^+$ after electrolysis at the appropriate potential in acetonitrile. In dichloromethane, the monocations can also be detected. But their conversion into $M(CO)_6$ has not been observed.

Cyclic voltammetric study of $Mo(\eta^6-C_7H_8)_2$ (**6**) shows that it undergoes a reversible 1-electron oxidation at $E_{1/2} = -0.43$ V vs ferrocenium-ferrocene couple. Chemical oxidation of **6** can be achieved by the action of $AgBF_4$, giving the cation $[Mo(\eta^6-C_7H_8)_2]^+$ (**8**). Reduction of **8** with sodium amalgam regenerates the neutral compound **6**.²¹

Oxidation of $Zr(\eta^6-C_7H_8)_2$ (**16**) with iodine in THF leads to the formation of $Zr(\eta^7-C_7H_7)(THF)_2I$ (**63**),^{26b,27} whereas reaction of **16** with $(AlEt_2Cl)_2$ in THF produces the dimer **64** (Scheme 33).²⁴

Treatment of $Zr(\eta^6-C_7H_8)(PMe_3)_2Cl_2$ (**65**) with an excess of lithium indenide affords a mixture of the sandwich compound $Zr(\eta^7-C_7H_7)(\eta^5-C_9H_7)$ (**66**) and its PMe_3 adduct **67** (Scheme 34). Recrystallization of the mixture in the presence of PMe_3 results in the isolation of pure **67**. This compound is thermally unstable and on heating under vacuum, it evolves

Scheme 35



PMe_3 to give **66**. The reaction with the hafnium analog $Hf(\eta^6-C_7H_8)(PMe_3)_2Cl_2$ (**68**) gives similar results, except that the hafnium phosphine adduct $Hf(\eta^7-C_7H_7)(\eta^5-C_9H_7)(PMe_3)$ is thermally more robust than its zirconium counterpart **67**.²⁸

Compounds **65** and **68** also react with sodium cyclopentadienide giving an inseparable mixture of isomers **69** and **70** (Scheme 35). The crystal structure of the major isomer **69** (M = Zr) reveals that the C_7H_8 ligand is η^2 -bonded to the metal by the C(3) and C(4) carbons. At elevated temperature, the reaction of **65** with sodium cyclopentadienide gives the dimer $[Zr(\eta^5-C_5H_5)(\mu-\sigma:\eta^5-C_5H_4)(PMe_3)_2]_2$ in 14% yield.²⁸

In contrast, the reaction of $Nb(\eta^6-C_7H_8)(PMe_3)_2Cl_2$ (**20**) with an excess of NaC_5H_4R (R = H or Me) yields the paramagnetic sandwich compounds $Nb(\eta^7-C_7H_7)-$

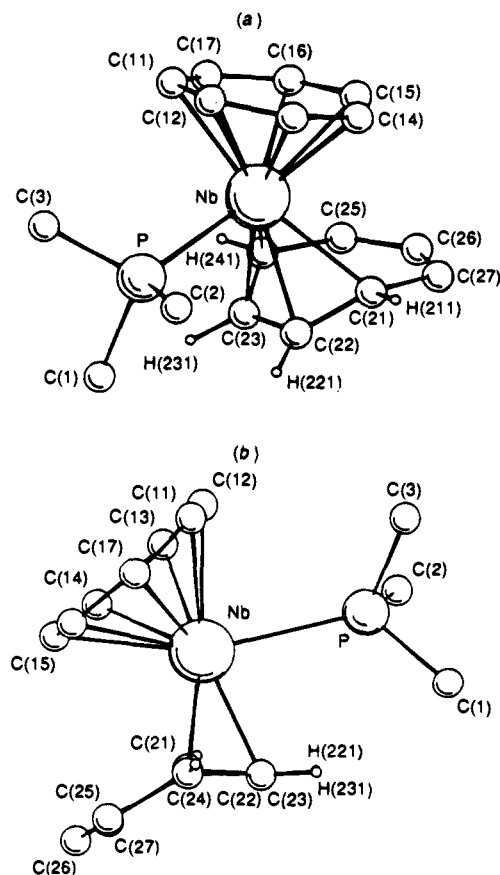
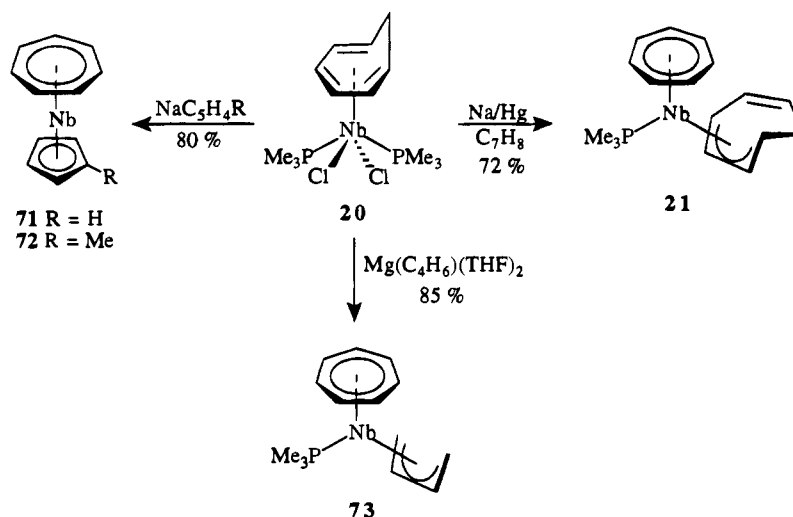
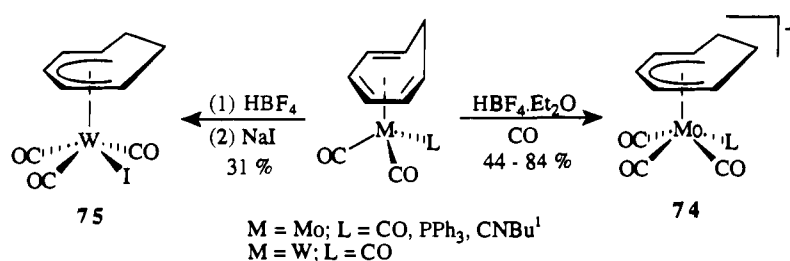


Figure 9. Molecular structure of $Nb(\eta^7-C_7H_7)(\eta^4-C_7H_8)(PMe_3)$. Most hydrogen atoms omitted.

Scheme 36



Scheme 37



(η^5 -C₅H₄R) [R = H (**71**) or Me (**72**)] as the sole product. Reduction of **20** with excess sodium amalgam and cycloheptatriene leads to the η^4 -cycloheptatriene complex **21** in good yield. Figure 9 shows the molecular structure of **21**, in which the coordinated C₄ fragment is essentially planar and the contribution of a metallacyclopentene structure in **21** is relatively small. Treatment of **20** with the magnesium butadiene complex Mg(C₄H₆)(THF)₂ causes reductive substitution of metal chlorides giving Nb(η^7 -C₇H₇)(η^4 -C₄H₆)(PMe₃) (**73**) (Scheme 36).³⁵

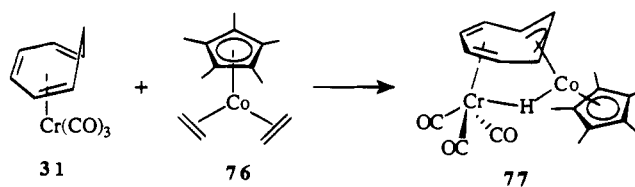
6. Other Reactions

Protonation of M(η^6 -C₇H₈)(CO)₃ [M = Mo (**43**) or W (**44**)] with HBF₄ produces the 16-electron cations [M(η^5 -C₇H₉)(CO)₃]⁺ while protonation with HCl leads to the formation of the neutral complexes M(η^5 -C₇H₉)(CO)₃Cl.⁹⁷ In the presence of a vigorous stream of carbon monoxide, the reaction of Mo(η^6 -C₇H₈)(CO)₂L (L = CO, PPh₃, or CNBu^t) with HBF₄.Et₂O gives the cycloheptadienyl cations [Mo(η^5 -C₇H₉)(CO)₃L]⁺ (**74**) (Scheme 37).^{98a,b} The tungsten analog of **74** cannot be obtained by this method. However, treatment of **44** with HBF₄ followed by reaction with NaI affords moderate yield of W(η^5 -C₇H₉)(CO)₃I (**75**) (Scheme 37).^{98a}

Addition of potassium triethyl borohydride to M(η^6 -C₇H₈)(CO)₃ [M = Cr (**31**) or Mo (**43**)] yields the salts [K][M(η^5 -C₇H₉)(CO)₃], which react with R₃SnCl (R = Me or Ph) and *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide to give M(η^5 -C₇H₉)(CO)₃SnR₃ and M(η^5 -C₇H₉)(CO)₂(NO), respectively.^{98c}

The reaction of **31** with Co(η^5 -C₅Me₅)(η^2 -C₂H₄)₂ (**76**) affords the unusual heterobimetallic complex **77** in 15–25% yield (Scheme 38).⁹⁹ The reaction involves

Scheme 38



a change in hapticity of the seven-membered ring, loss of ethene, and a hydrogen shift. Upon treatment with CO, compound **77** regenerates **31** and gives Co(η^5 -C₅Me₅)(CO)₂. The structure of **77** (Figure 10) shows that the bridging cycloheptatriene bonds to the Cr and Co in a η^4 - and η^3 -manner, respectively, and adopts a boat conformation. A bridging hydrogen is also present which allows both metals to attain an 18-electron configuration. Low-temperature ¹H and

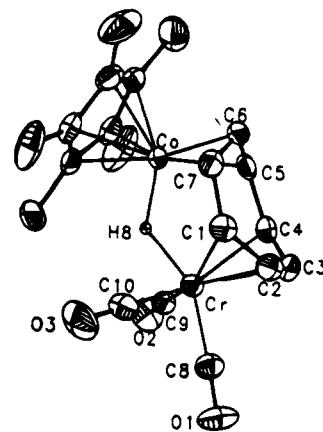
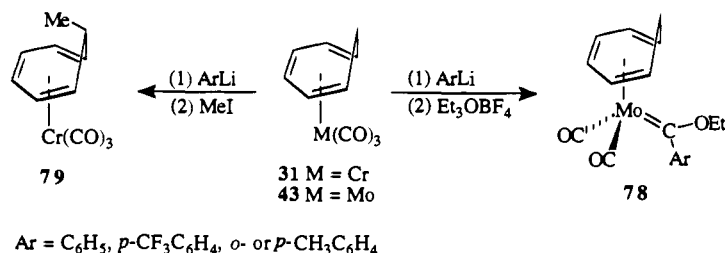


Figure 10. Molecular structure of Cr(CO)₃(μ - η^4 : η^3 -C₇H₇)(μ -H)Co(η^5 -C₅Me₅).

Scheme 39



¹³C NMR spectra of **77** exhibit signal patterns corresponding to a rigid $\mu\text{-}\eta^4\text{:}\eta^3\text{-C}_7\text{H}_7$ structure. This is in contrast to those of the related *syn*-M($\mu\text{-C}_7\text{H}_7$)M' complexes in which the rotation of the C₇H₇ ring cannot be frozen out.¹⁰⁰

Treatment of **43** with aryllithium at low temperature followed by the addition of Et₃OBF₄ gives the cycloheptatriene carbene complexes **78** (Scheme 39). For the chromium analog **31**, the reaction proceeds only with *p*-CF₃C₆H₄Li. Other aryllithium compounds, such as C₆H₅Li, *o*- or *p*-CH₃C₆H₄Li, cause deprotonation at the C(7) carbon atom of the cycloheptatriene ring giving *exo*-Cr($\eta^6\text{-C}_7\text{H}_7\text{Li-7}$)(CO)₃. Alkylation with iodomethane gives the substituted cycloheptatriene complex **79** (Scheme 39).^{101a}

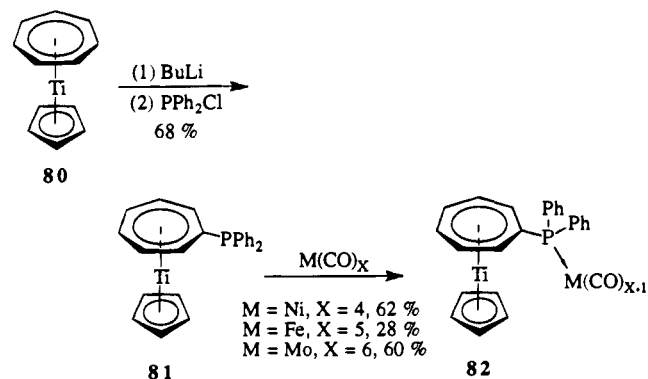
The gas-phase ion chemistry of **31** has recently been studied by Fourier transform ion cyclotron resonance spectroscopy.^{101b} The ion reactivities parallel the electron deficiencies of the central metal atoms and show the order Cr⁺ > C₅H₆Cr⁺ > C₇H₈Cr⁺ ≈ C₇H₈Cr(CO)⁺ > C₇H₈Cr(CO)₂⁺ > C₇H₈Cr(CO)₃⁺. The ion C₇H₈Cr⁺ has an anomalously low reactivity which has been explained by a β -hydride shift from the cycloheptatriene ring to the chromium atom that decreases the electron deficiency on the central metal.

B. Cycloheptatrienyl Metal Complexes

1. Lithiation Reactions

It was reported that lithiation of the sandwich compound Ti($\eta^7\text{-C}_7\text{H}_7$)($\eta^5\text{-C}_5\text{H}_5$) (**80**) occurs preferentially at the seven-membered ring. Addition of electrophile to the resulting lithiated species leads to selective functionalization of the cycloheptatrienyl ligand.⁵⁷ Thus treatment of **80** with 1 equiv of *n*-butyllithium in ether followed by the addition of 1 equiv of PPh₂Cl affords the phosphine containing titanium compound **81** (Scheme 40). The phosphorus group in **81** retains its nucleophilic and coordinating properties and its donating capability is slightly

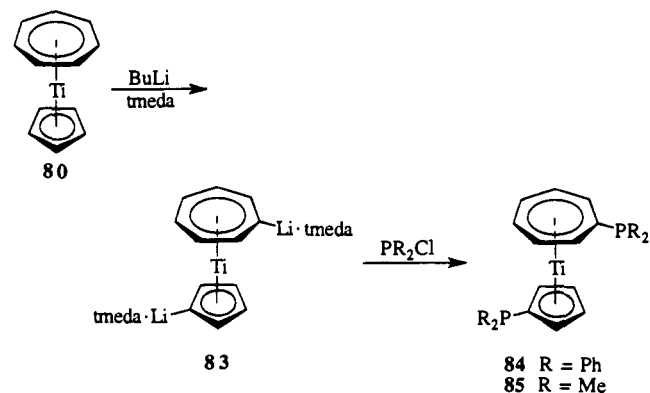
Scheme 40



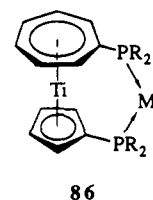
stronger than that of PPh₃. It displaces one carbonyl of Ni(CO)₄, Fe(CO)₅, and Mo(CO)₆ forming the bimetallic complexes **82** (Scheme 40).¹⁰²

Dimetalation of **80** can be achieved with 2.5 equiv of butyllithium–tmeda in hexane giving the highly air-sensitive dilithium derivative **83**. A subsequent reaction between **83** and 2 equiv of PR₂Cl (R = Ph¹⁰³ or Me¹⁰⁴) produces diphosphines **84** or **85** (Scheme 41). These compounds react with various metal

Scheme 41

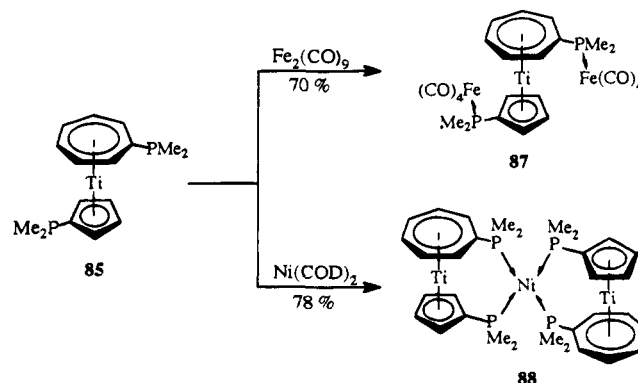


carbonyls of Cr, Mo, Mn,¹⁰⁵ Fe, and Co to produce a series of chelated heterobimetallic compounds Ti($\eta^7\text{-C}_7\text{H}_6\text{PR}_2$)($\eta^5\text{-C}_5\text{H}_4\text{PR}_2$)M' (**86**) [for R = Ph, M' = Cr-

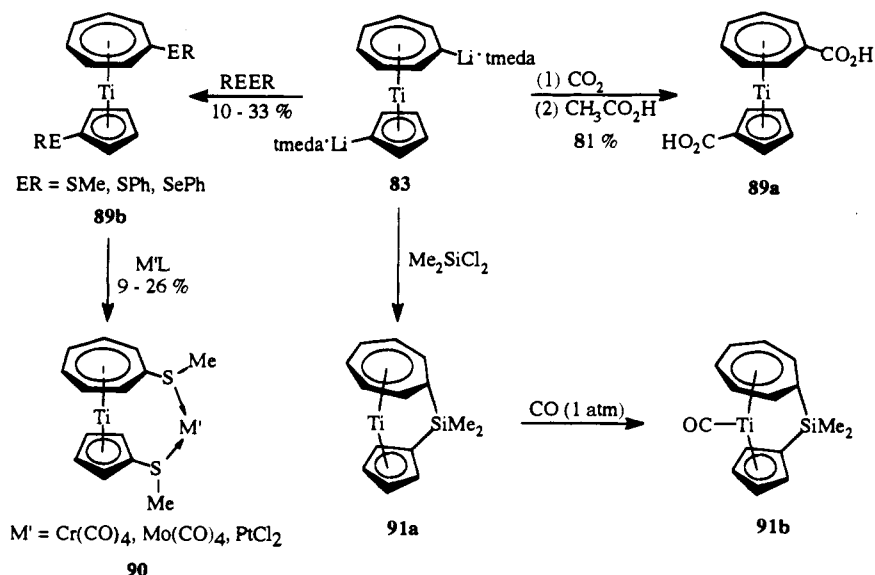


(CO)₄, Mo(CO)₄, Mn(CO)₃H, Fe(CO)₃ or Co($\eta^5\text{-C}_5\text{H}_5$); for R = Me, M' = Cr(CO)₄ or Mo(CO)₄]. However, reaction between **85** and Fe₂(CO)₉ under similar

Scheme 42



Scheme 43



conditions gives the nonchelated product **87**. The phosphine ligands in **85** can also displace the COD ligands in Ni(COD)₂ giving the Ni(0) complex **88** (Scheme 42). The molecular structures of Ti(η⁷-C₇H₆-PR₂)(η⁵-C₅H₄PR₂)Cr(CO)₄ (R = Ph or Me) and Ti(η⁷-C₇H₆PPh₂)(η⁵-C₅H₄PPh₂)Mn(CO)₃H have been elucidated, which show the insensitivity of the titanium sandwich structure to coordination of the phosphine ligands.¹⁰³⁻¹⁰⁵

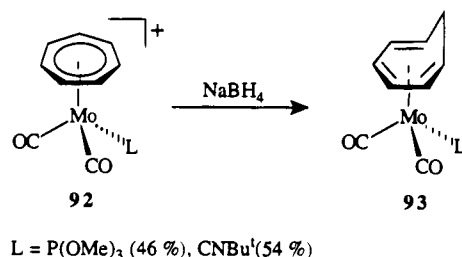
The mono- and dilithiated derivatives of **80** also react with other electrophiles.^{106,107} For example, treatment of **83** with CO₂ followed by acidification gives the diacid **89a**,^{106a} whereas the reaction of **83** with RSSR (R = Me or Ph) or PhSeSePh produces the sulfur or selenium derivatives **89b**.^{106b} Compound **89b** (ER = SMe) reacts with M(η⁴-norbornadiene)(CO)₄ (M = Cr or Mo) or Pt(C₆H₅CN)₂Cl₂, giving the chelated complexes **90**. Treatment of **83** with Me₂SiCl₂ leads to the dimethylsilyl-bridged complex **91a**, which reacts with CO at ambient pressure to form the monocarbonyl complex **91b** (Scheme 43). It is worth noting that **80** does not carbonylate even at 14000 kPa.¹⁰⁷

2. Nucleophilic Attack on η-C₇H₇ Ring

The C₇ ring in cationic cycloheptatrienyl complexes is susceptible to nucleophilic attack. For example, treatment of [Mo(η⁷-C₇H₇)(CO)₂L]⁺ [L = P(OMe)₃ or CNBu^t] (**92**) with NaBH₄ results in the formation of Mo(η⁶-C₇H₈)(CO)₂L (**93**) (Scheme 44).^{98b,108} Substitution of CO in [Mo(η⁷-C₇H₇)(CO)₃]⁺ with a σ-donor L followed by nucleophilic attack is a commonly used method to prepare the otherwise inaccessible L-substituted compounds Mo(η⁶-C₇H₇R-7)(CO)₂L (R = H or alkyl).¹⁰⁹

Substituted anilines, XC₆H₄NH₂ (X = H, 2-Me, 4-Me, or 2-Cl), add to the C₇ ring of [W(η⁷-C₇H₇)(CO)₃]⁺ (**94**) giving the corresponding cycloheptatriene adducts W(η⁶-C₇H₇-NHC₆H₄X-7)(CO)₃ (**95**). Kinetic studies show that the reactions occur via a rapid preequilibrium formation of a π-complex followed by a rate-determining rearrangement to the cationic triene intermediate **96**, which rapidly loses

Scheme 44

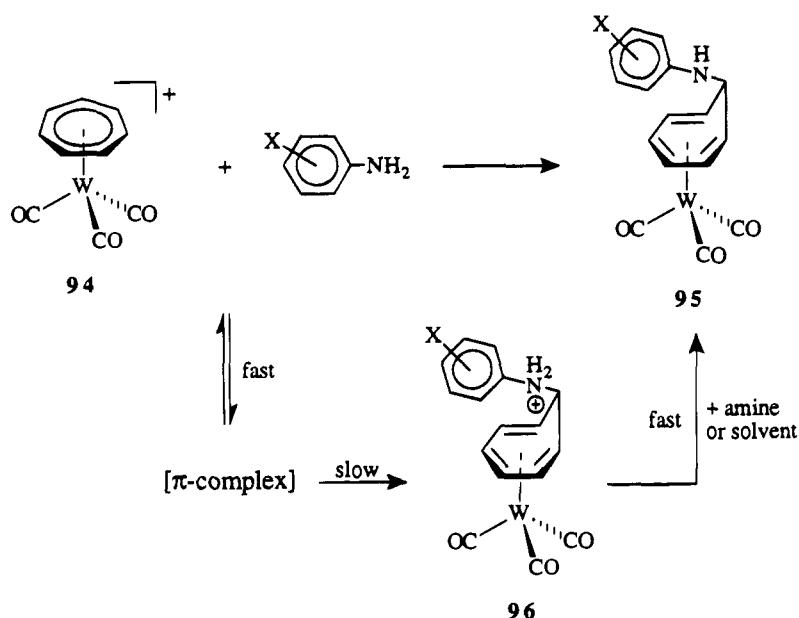


a proton with the aid of amine or solvent to form the product **95** (Scheme 45). For the reaction with cyclohexylamine, the cationic intermediate is formed directly in a rapid preequilibrium, followed by competing rate-determining amine- and solvent-assisted proton removal.¹¹⁰

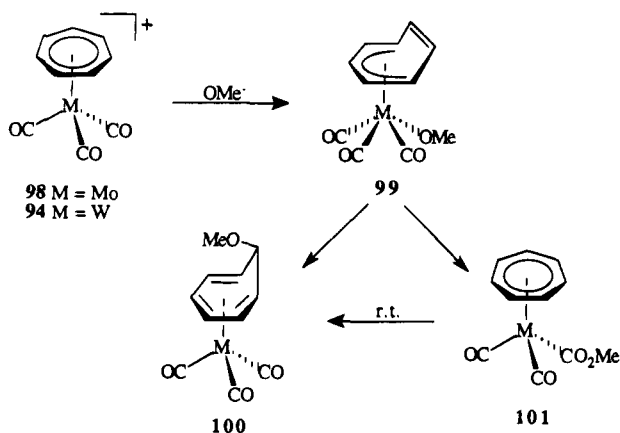
The reaction of [M(η⁷-C₇H₇)(CO)₃]⁺ [M = Cr (**97**), Mo (**98**), or W (**94**)] with methoxide ion has been studied in detail. Low-temperature IR and NMR spectroscopy have revealed that the reactions for Mo and W involve an initial attack at the metal forming **99** followed by dissociation to give both the thermodynamically stable 7-*exo* adducts **100** and the carbomethoxy species **101**. The latter compounds are quite stable at low temperature, but rearrange to **100** at room temperature (Scheme 46). The related chromium analogs of **99** and **101** could not be detected.¹¹¹ Theoretical calculations have also predicted the initial metal attack for these reactions.¹¹² Further evidences have been provided by the kinetic studies with stopped-flow spectrophotometry. Two separate processes have been identified. The first one involves a fast reversible formation of either **99** or **101**, while the second slower process involves methoxy ion attack to the C₇ ring for which the second rate constants are in the ratio 50:10:1 (Cr:Mo:W).¹¹³

The relative rates of methoxide ion transfer from methoxymalachite green (*p*-Me₂NC₆H₄)₂CPhOMe to **97**, **98**, and **94** are 1:10:6 (Cr:Mo:W), which are much slower than that of the reaction between C₇H₇⁺ and methoxide (*k*₂^{rel} = 110).¹¹⁴ π-Complexation of the C₇H₇⁺ cation with a Cr(CO)₃ also greatly reduces its

Scheme 45

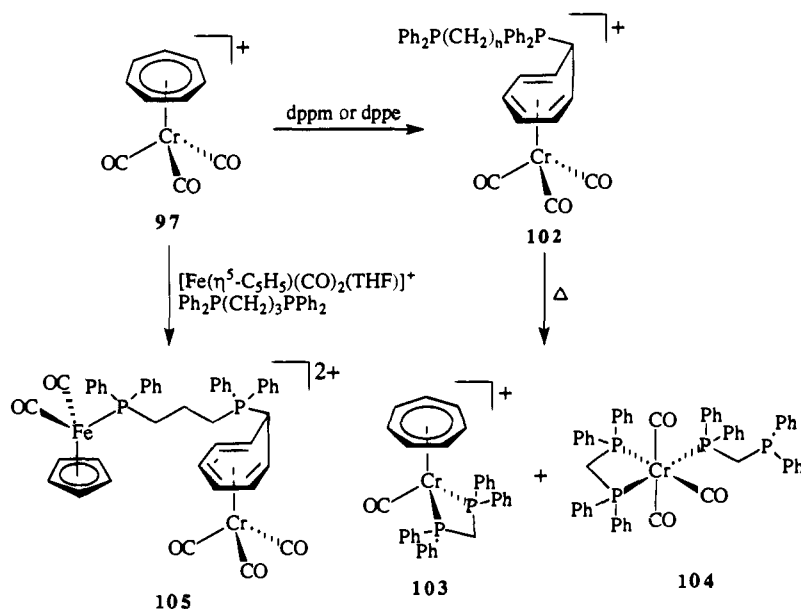


Scheme 46



reactivity toward addition of methanol. The rate constant for this reaction as well as its reverse

Scheme 47

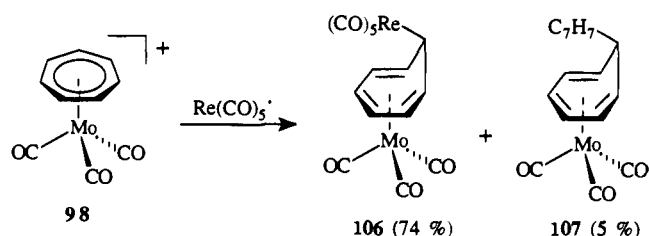


process, protonation of the 7-*exo* methoxy derivative, have been determined.¹¹⁵

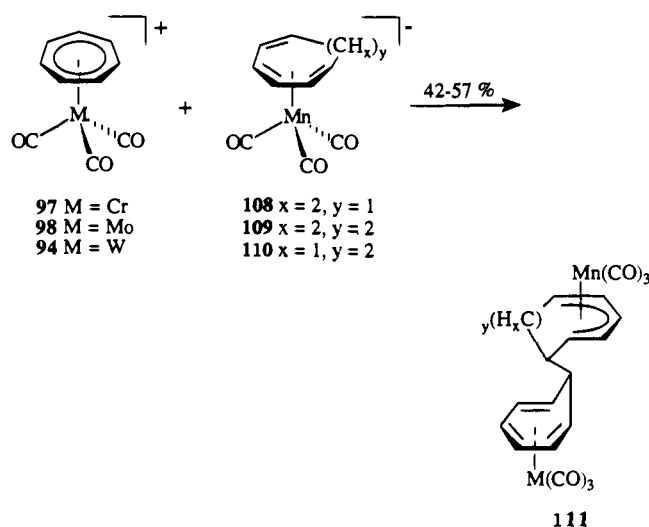
Treatment of $[\text{Cr}(\eta^7\text{-C}_7\text{H}_7)(\text{CO})_3]^+$ (**97**) with dppm (or dppe) in acetone at room temperature gives the *exo*-adduct **102**. ³¹P NMR data confirm the presence of a ring-bonded phosphorus ($\delta +20.8$) and a pendant phosphorus ($\delta -27.8$). Upon heating, compound **102** ($n = 1$) converts into a mixture of carbonyl substituted product **103** and ring substituted product **104**. Interestingly, the reaction of **97** with $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{THF})]^+$ and $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$ affords the diphosphine bridged dication **105** (Scheme 47).¹¹⁶

Recently, the addition of a variety of functionalized zinc-copper reagents $\text{RCu}(\text{CN})\text{ZnI}$ [$\text{R} = (\text{CH}_2)_n\text{CO}_2\text{-Et}$ ($n = 2-4$), $(\text{CH}_2)_n\text{CN}$ ($n = 2-4$), CH_2Ph , or $\text{CH}_2\text{-CH=CH}_2$] to **97** has been reported. The reactions give high yields of η^6 -cycloheptatriene complexes with a functionalized side chain at the C7 position of the ring. Upon treatment with lithium diisopropylamide,

Scheme 48



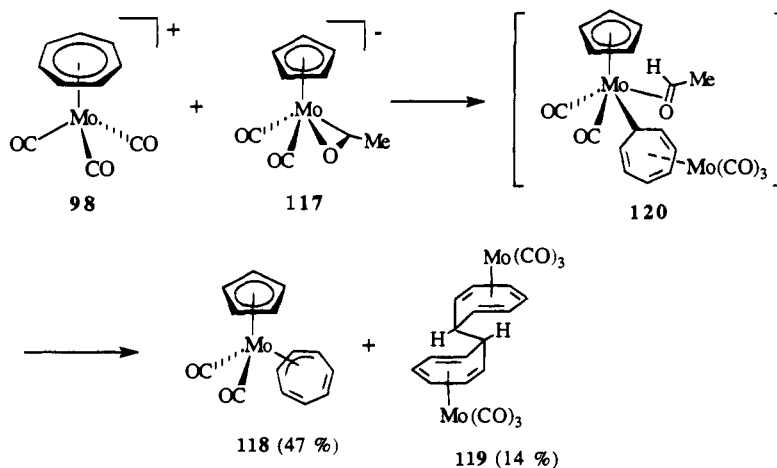
Scheme 49



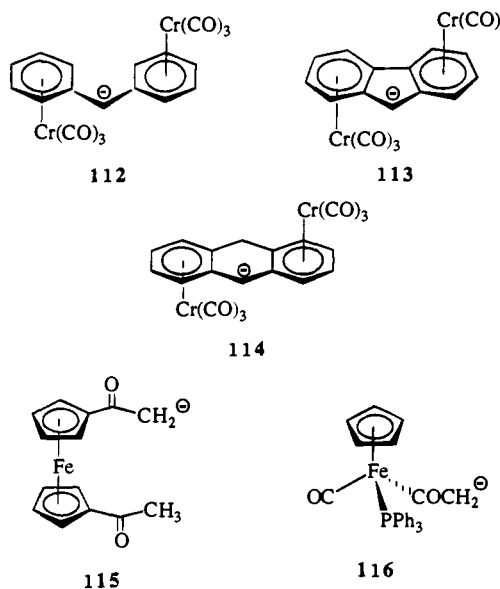
the ester-substituted adducts undergo intramolecular cyclization generating fused bicyclo[5.3.0]decane and -[5.4.0]undecane derivatives.¹¹⁷

The addition of organometallic nucleophiles to **97**, **98**, and **94** has also been reported. Treatment of **98** with $[\text{Re}(\text{CO})_5]^+$ gives the expected adduct **106** with small amount of **107** (Scheme 48). Both of these complexes have been structurally characterized.¹¹⁸ The addition of dianions $[\text{M}'(\text{CO})_4]^{2-}$ ($\text{M}' = \text{Os}$ or Ru) to **97** or **98** leads to the heterotrimeric complexes *cis*- $\text{M}'(\text{CO})_4[\text{M}(\mu\text{-}\eta^1\text{-}\eta^6\text{-C}_7\text{H}_7)(\text{CO})_3]_2$. For the complex with $\text{M} = \text{Mo}$, $\text{M}' = \text{Os}$, the crystal structure has been determined.¹¹⁹ The reaction of **97**, **98**, and **94** with $[\text{Mn}(\eta^4\text{-C}_7\text{H}_8)(\text{CO})_3]^-$ (**108**), $[\text{Mn}(\eta^4\text{-C}_8\text{H}_{10})(\text{CO})_3]^-$ (**109**), or $[\text{Mn}(\eta^4\text{-C}_8\text{H}_8)(\text{CO})_3]^-$ (**110**) results in coupling of the ring ligands, giving the hydrocarbon-bridged complexes **111** (Scheme 49).¹²⁰ Other nucleophiles,

Scheme 50



such as **112**–**116**, also attack the C_7 ring of **97**, **98**, and **94** forming the *exo*-isomer of the adducts.^{121,122}



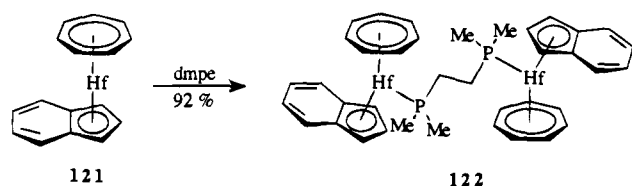
Treatment of **98** with the complexed acetaldehyde anion **117** gives a mixture of products from which **118** and **119** can be isolated. The formation of **118** and **119** arise from the intermediate **120** formed by nucleophilic attack of the anion **117** at the C_7 ring of **98**. As the η^3 -tropylium interaction is formed, the aldehyde and $\text{Mo}(\text{CO})_3$ fragments are lost in **120** leading to **118** (Scheme 50).¹²³

3. Lewis Base Addition and Ring Slippage Reactions

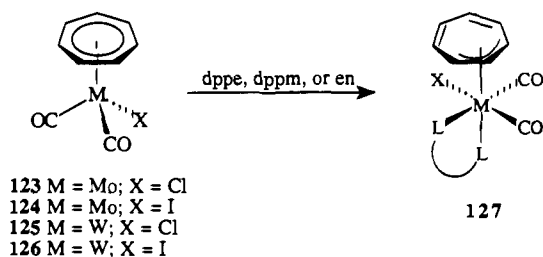
The coordinatively unsaturated mixed-sandwich compounds $\text{M}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_9\text{H}_7)$ [$\text{M} = \text{Zr}$ (**66**) or Hf (**121**)], upon treatment with PMe_3 , are transformed into the 18-electron complexes $\text{M}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_9\text{H}_7)(\text{PMe}_3)$. With the bidentate dmpe, the hafnium complex **121** converts into the bridged dimer **122** of which the crystal structure has been determined (Scheme 51).²⁸

Addition of Lewis bases to coordinatively saturated complexes may induce a hapticity change of the C_7 ring. Thus the complexes $\text{M}(\eta^7\text{-C}_7\text{H}_7)(\text{CO})_2\text{X}$ ($\text{M} = \text{Mo}$ or W ; $\text{X} = \text{Cl}$ or I) **123**–**126** react with bidentate ligands, such as dppe, dppm, or en giving the trihapto

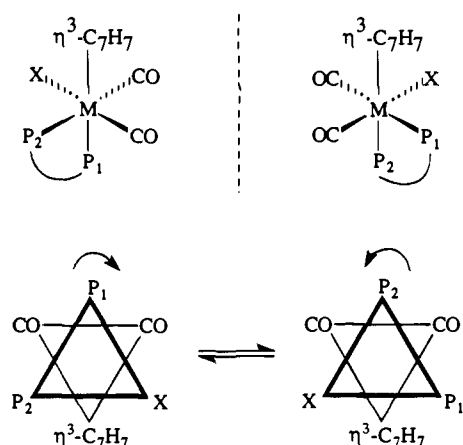
Scheme 51



Scheme 52



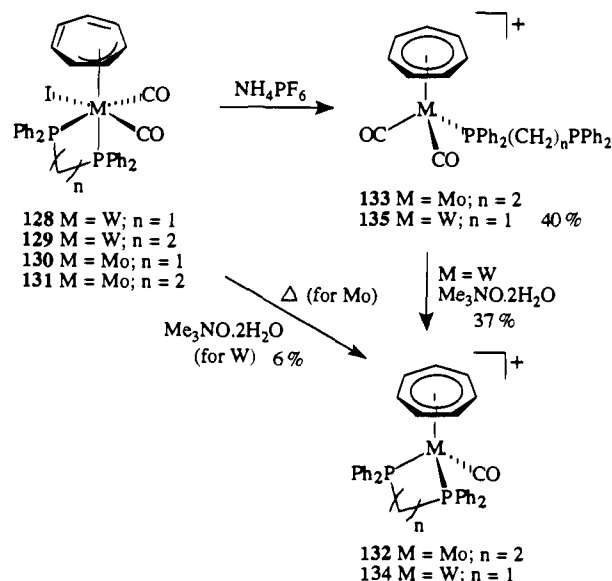
Scheme 53



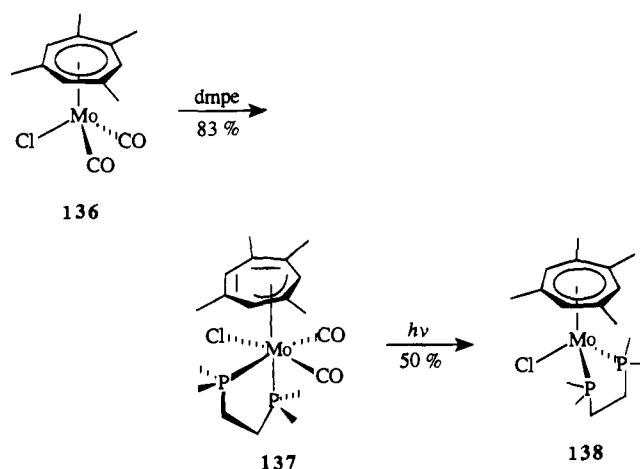
complexes **127** (Scheme 52).¹²⁴⁻¹²⁶ All of these compounds undergo 1,2-shift of metal around the C₇ ring, so only one ¹H NMR resonance is observed for the C₇ ring protons. For the en complexes, this 1,2-shift process can be frozen out at low temperature and the individual environments of the η³-C₇H₇ ring can be resolved. The dppe complexes also exhibit a fluxional process which interconverts inequivalent phosphorus environments. A trigonal twist rearrangement has been proposed for this process (Scheme 53).¹²⁶ The diene moiety in the η³-C₇H₇ ligand of the tungsten complexes W(η³-C₇H₇)(CO)₂(L-L)I [L-L = dppm (**128**) or dppe (**129**)] undergoes a Diels-Alder reaction with TCNE forming the corresponding adducts.¹²⁶

The tungsten complexes **128** and **129** are more stable than the molybdenum analogs **130** and **131** with respect to loss of CO and conversion to η⁷-cycloheptatrienyl derivatives.^{124,125} Thus, while compound **131** converts to **132** readily in refluxing benzene, the tungsten compound **129** is stable even in refluxing toluene. Similarly, treatment of **131** with an excess of NH₄PF₆ gives the η¹-dppe complex **133**, but the tungsten analog **129** remains intact under these conditions. However, compound **128**, with a strained four-membered metal chelate ring, does react slowly with Me₃NO·2H₂O to give **134**, and with NH₄PF₆ to give **135**. The former compound is better prepared by treating the latter compound with Me₃NO·2H₂O (Scheme 54).

Scheme 54



Scheme 55

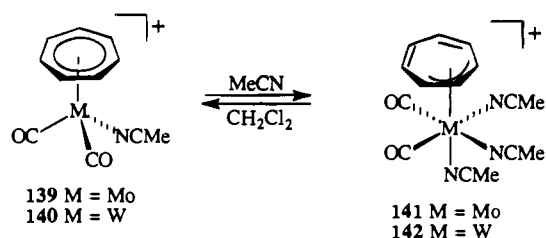


The tetramethylcycloheptatrienyl molybdenum complex Mo(η⁷-C₇H₃Me₄-1,2,4,6)(CO)₂Cl (**136**) reacts with dmpe in a similar manner giving the trihapto complex **137**. Variable-temperature NMR studies have shown that this complex is fluxional due to trigonal twist rearrangement and 1,2-shift of metal around the C₇ ring. The value of ΔG[‡] for the former process has been estimated to be 53.3 kJ/mol. Upon photolysis, displacement of CO ligands occurs with the formation of η⁷-cycloheptatrienyl complex **138** (Scheme 55).¹²

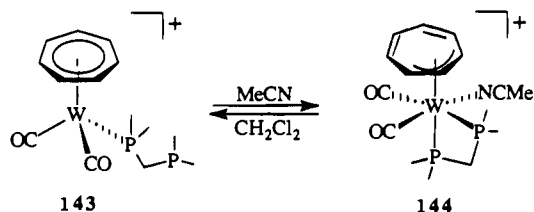
The cations [M(η⁷-C₇H₇)(CO)₂(MeCN)]⁺ [M = Mo (**139**) or W (**140**)] also undergo hapticity change in acetonitrile solution giving the trisacetonitrile complexes **141** and **142**, which are the first examples of a cationic η³-C₇H₇ species. In weak coordinating solvents, such as dichloromethane and THF, displacement of two acetonitrile ligands from **141** and **142** is accompanied by reversion to a heptahapto-bonded cycloheptatrienyl ring (Scheme 56).^{108,127} The interconversion of related complexes **143** and **144** has also been established (Scheme 57).¹⁰⁸

The analogous cationic carbonylisonitrile complexes **145** and **146** also undergo η⁷-η³ ring slippage on addition of CNBu^t. However, the reversion of

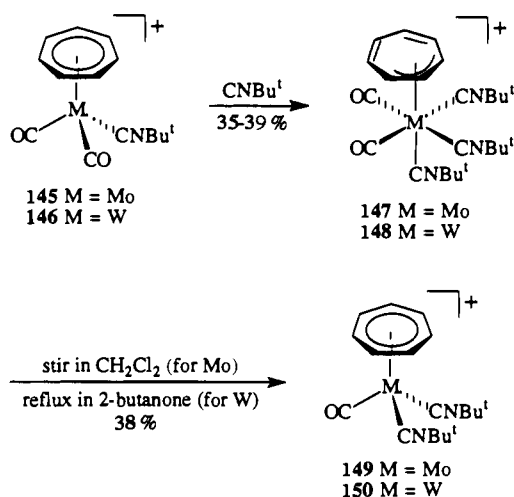
Scheme 56



Scheme 57



Scheme 58

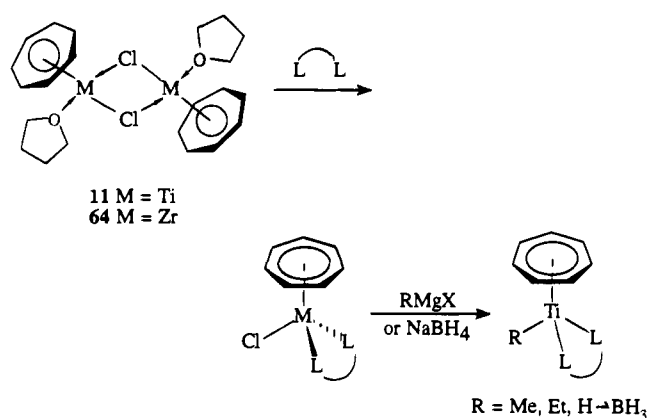


trihapto complexes **147** and **148** to products with a heptahapto-bonded C₇ ring involves loss of one CNBu^t ligand and one CO ligand (Scheme 58), which is in contrast to the case of acetonitrile analogs.¹²⁸ Compounds **149** and **150** are the formal substitution products of **145** and **146** with CNBu^t, thus the reaction sequence shown in Scheme 58 provides a well-defined example of ligand substitution at the metal center of cycloheptatrienyl complexes proceeding via an η³-C₇H₇ intermediate. In an excess of CNBu^t, the molybdenum compound **149** undergoes further ring slip giving [Mo(η³-C₇H₇)(CO)(CNBu^t)₄]⁺, which upon heating, converts to a mixture of **149** and the substituted product [Mo(η⁷-C₇H₇)(CNBu^t)₃]⁺.¹²⁸

4. Ligand Exchange Reactions

The readily accessible binuclear compounds [M(η⁷-C₇H₇)(THF)(μ-Cl)]₂ [M = Ti (**11**) or Zr (**64**)] are good precursors toward cycloheptatrienyl derivatives of titanium and zirconium. They undergo bridge-splitting reactions upon treatment with a wide range of O-, N-, and P-donor ligands, such as dme, tmeda, PMe₃, dmpe, dppe, dippe, and *trans*-1,2-bis(dimethylphosphino)cyclopentane, forming the monomeric species M(η⁷-C₇H₇)(L-L)Cl. Reaction of alkyl Grignard reagents or NaBH₄ with the appropriate titanium chloro derivatives gives the corresponding

Scheme 59



alkylated or single bridging M-H→BH₃ compounds (Scheme 59).^{22,24} The THF ligands in Zr(η⁷-C₇H₇)(THF)₂I (**63**) can also be displaced by PMe₃ giving the complex Zr(η⁷-C₇H₇)(PMe₃)₂I.^{26b,27}

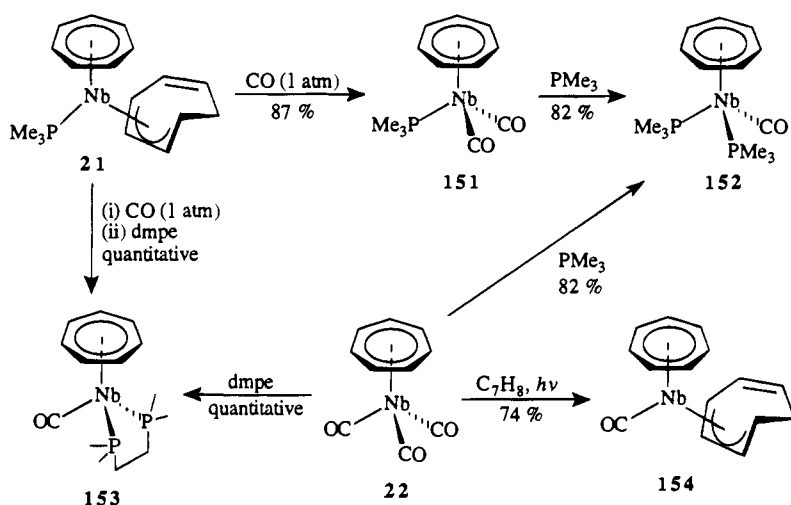
The η⁴-C₇H₈ ligand in niobium complex Nb(η⁷-C₇H₇)(η⁴-C₇H₈)(PMe₃) (**21**) is labile and can be replaced by CO ligands. The resulting complex **151** undergoes further substitution with PMe₃ and dmpe. The former reaction gives bis(trimethylphosphine) product **152** while the latter reaction leads to substitution of CO and PMe₃ forming **153**. The compounds **152** and **153** can also be prepared by treating the tricarbonyl complex Nb(η⁷-C₇H₇)(CO)₃ (**22**) with the corresponding phosphines. Under photolysis, **22** reacts with an excess of cycloheptatriene affording **154** (Scheme 60).³⁵ This is analogous with the photochemical reaction of Nb(η⁵-C₅H₅)(CO)₄ in the presence of cycloheptatriene, which gives Nb(η⁵-C₅H₅)(η⁴-C₇H₈)(CO)₂.¹²⁹

The η⁷-C₇H₇ group normally acts as a robust, nonlabile ligand. However, displacement of C₇ ring in cycloheptatrienyl complexes has been reported. Treatment of Ti(η⁷-C₇H₇)(η⁵-C₅H₅) (**80**) with dithioacetic acid gives Ti(η⁵-C₅H₅)(S₂CCH₃)₃ (**155**), while similar reaction on Nb(η⁷-C₇H₇)(η⁵-C₅H₅) (**71**) affords Nb(η⁵-C₅H₅)(S₂CCH₃)₂(η²-S₂) (**156**) (Scheme 61). The crystal structures of both of these seven-coordinate molecules have been reported.³⁸ The reaction of **80** with trifluoroacetic acid, however, leads to the formation of trifluoroacetate bridged dimer [Ti(η⁵-C₅H₅)₂(μ-CF₃CO₂)₄] in 65% yield.¹³⁰

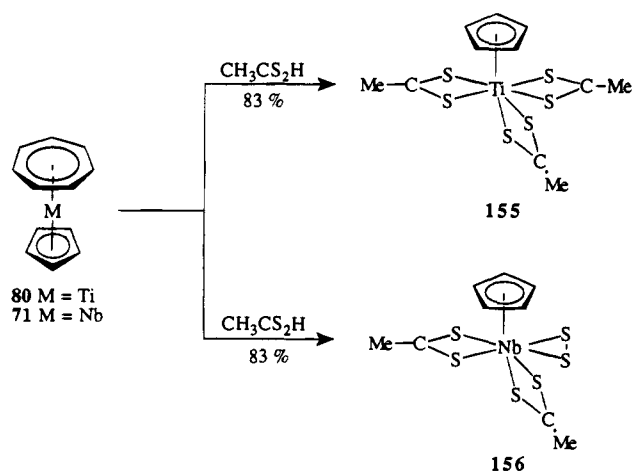
The reaction of [M(η⁷-C₇H₇)(CO)₃]⁺ [M = Cr (**97**), Mo (**98**), or W (**94**)] with phosphines leads to nucleophilic attack on the ring,¹³¹ substitution of CO ligand,^{109,132} or displacement of the ring¹³³ depending on the reaction conditions, the nature of the nucleophile and the metal center. With excess PPh₃, the tungsten cation **94** is transformed into *fac*-W(PPh₃)₃(CO)₃. Kinetic studies have showed that the reaction involves rapid preequilibrium formation of a π-complex, followed by rate-determining attack by a second PPh₃ molecule at the metal. Subsequent attack by a third PPh₃ at the metal results in rapid displacement of the C₇ ring to give the product.¹³⁴ Treatment of **98** or **94** with the η¹-dppe molybdenum complex [Mo(η⁷-C₇H₇)(CO)₂(η¹-dppe)]⁺ (**133**) results in CO substitution yielding the dppe-bridged dication [M(η⁷-C₇H₇)(CO)₂(μ-dppe)Mo(η⁷-C₇H₇)(CO)₂]²⁺.¹²⁵

The complexes M(η⁷-C₇H₇)(CO)₂X (M = Mo or W, X = halide) are key compounds in generating other

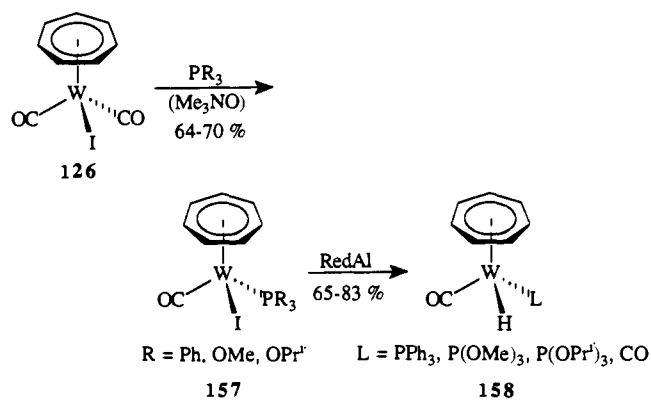
Scheme 60



Scheme 61

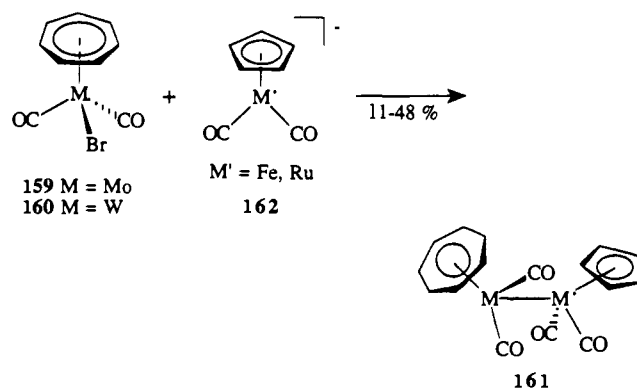


Scheme 62



cycloheptatrienyl molybdenum and tungsten complexes. They undergo halide and/or CO substitution with a variety of reagents. For example, treatment of $W(\eta^7\text{-C}_7\text{H}_7)(\text{CO})_2\text{I}$ (**126**) with PPh_3 gives the mono-substituted product **157** ($\text{R} = \text{Ph}$).¹³⁵ For the reaction with phosphites $\text{P}(\text{OMe})_3$ and $\text{P}(\text{OPr}^i)_3$, compound Me_3NO is also added for decarbonylation.⁴³ Both **126** and **157** react with sodium dihydrido-bis(2-methoxyethoxy)aluminum (RedAl) to give the corresponding tungsten hydride complexes **158** (Scheme 62). The tetramethylcycloheptatrienyl analogs $W(\eta^7\text{-C}_7\text{H}_7\text{Me}_4\text{-1,2,4,6})(\text{CO})_2\text{X}$ ($\text{X} = \text{Br}$ or I), prepared from the

Scheme 63



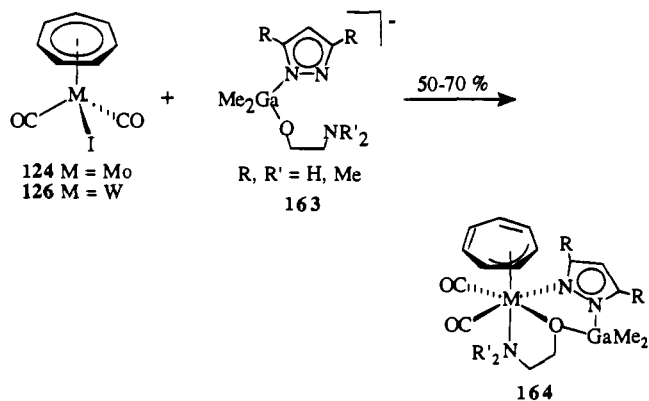
reaction of tricarbonyl cation $[W(\eta^7\text{-C}_7\text{H}_7\text{Me}_4\text{-1,2,4,6})(\text{CO})_3]^+$ and $[\text{Bu}_4\text{N}][\text{X}]$, react with the phosphorus-donor ligands and sequence RedAl in a similar manner.⁴³

The molybdenum complex $\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{CO})_2\text{Br}$ (**159**) also reacts with PR_3 ($\text{R} = \text{Me}$ or Ph) to give the CO substitution products $\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{CO})(\text{PR}_3)\text{Br}$, which, upon treatment with appropriate organolithium or Grignard reagents, generate $\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{CO})(\text{PR}_3)\text{R}'$ ($\text{R}' = \text{Me}, \text{Ph}, \text{C}_6\text{F}_5, \text{CH}=\text{CH}_2, \text{C}\equiv\text{CPh}, \text{or } \text{C}\equiv\text{CBu}^t$).¹³⁶

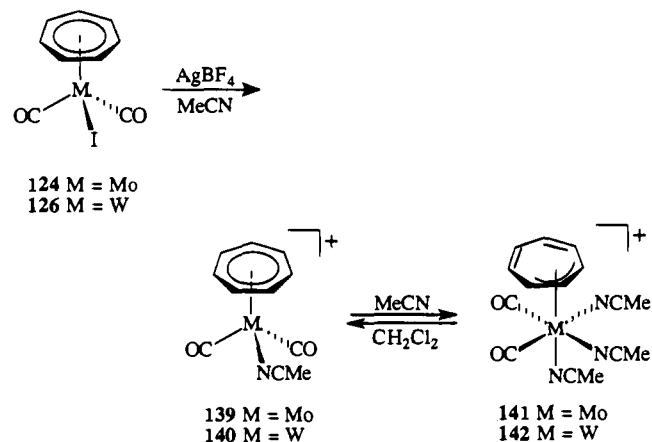
Displacement of halide in $M(\eta^7\text{-C}_7\text{H}_7)(\text{CO})_2\text{X}$ ($\text{M} = \text{Mo}$ or W ; $\text{X} = \text{halide}$) with nucleophiles is well-documented.¹³⁷ For example, reaction of **159** with RLi ($\text{R} = \text{Me}$ or Ph) gives the products $\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{CO})_2\text{R}$, which undergo SO_2 insertion into the $\text{Mo}-\text{C}(\text{R})$ bond. For $\text{R} = \text{Me}$, insertion of SeO_2 , TeO_2 , and Zn was also observed.¹³⁸

Recently, the heterobimetallic complexes $M(\eta^7\text{-C}_7\text{H}_7)(\text{CO})_2\text{M}'(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2$ ($\text{M} = \text{Mo}$ or W ; $\text{M}' = \text{Fe}$ or Ru) (**161**) have been prepared by treating **159** or **160** with $[\text{Na}][\text{M}'(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$ (**162**) (Scheme 63).¹³⁹ The molecular structure of **161** ($\text{M} = \text{Mo}$; $\text{M}' = \text{Ru}$) reveals an unsupported $\text{Mo}-\text{Ru}$ bond and a *cis* arrangement of C_5 and C_7 rings. However, solution infrared studies show that the conformation is solvent-dependent. In addition, the ambient-temperature ¹³C NMR spectra of **161** display only a single resonance for the carbonyl carbons. This observation has been attributed to an intermetallic carbonyl scrambling process. The reaction of **159** with $[\text{K}][\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2]$ gives the metal-metal bonded complex in very

Scheme 64



Scheme 65



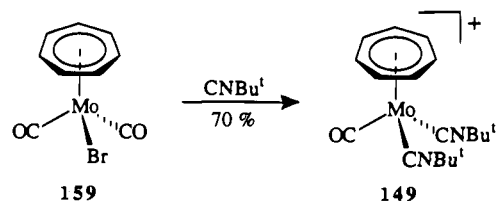
low yield together with the unexpected, but structurally characterized, $\text{Mo}(\text{CO})_3(\mu\text{-}\eta^6, \eta^1\text{-C}_7\text{H}_7)\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2$ as the major product.¹³⁹

Treatment of **124** or **126** with the novel ligands **163** results in displacement of iodide together with a $\eta^7\text{-}\eta^3$ hapticity change. The products **164** are pseudo octahedral with the organogallate ligands occupying a set of facial positions and the $\eta^3\text{-C}_7\text{H}_7$ ring situated opposite to the nitrogen atom (Scheme 64).¹⁴⁰ This has been confirmed by the X-ray crystal structure of **164** (M = Mo; R = Me; R' = H).¹⁴¹

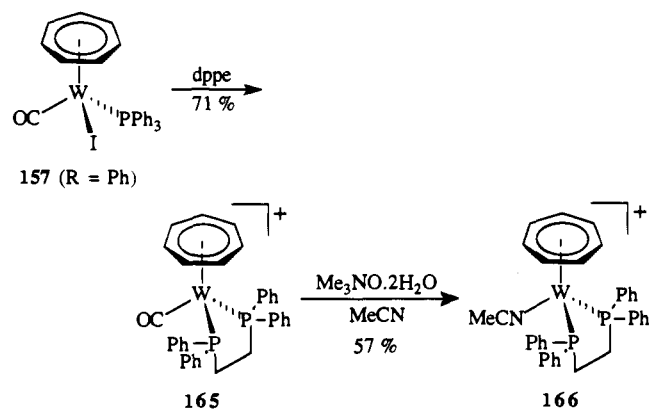
Reaction of **126** with AgBF_4 in acetonitrile gives the trihapto-cycloheptatrienyl complex **142**, which in CH_2Cl_2 is converted into **140**. As mentioned in section VI.B.3, dissolution of **140** in acetonitrile results in rapid reformation of **142**, indicating that **140** is the actual first product in this reaction. A similar reaction sequence has been observed for the molybdenum complex **124** but an equilibrium mixture of **139** and **141** is produced. Removal of acetonitrile and dissolution of the residue in CH_2Cl_2 gives **139** as the sole product (Scheme 65). The benzonitrile analog $[\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{CO})_2(\text{NCPh})]^+$ has also been prepared similarly.^{108,127} Two of the acetonitrile ligands in **141** and **142** can be displaced by dppe giving $[\text{M}(\eta^3\text{-C}_7\text{H}_7)(\text{CO})_2(\text{dppe})(\text{MeCN})]^+$ (M = Mo or W).^{108,127}

Displacement of halide in $\text{M}(\eta^7\text{-C}_7\text{H}_7)(\text{CO})_2\text{X}$ (M = Mo or W; X = halide) may also accompany CO substitution. For example, treatment of **159** with 2 equiv of CNBu^t gives **149** in high yield (Scheme 66).¹²⁸ Similarly, the compound **157** (R = Ph), upon

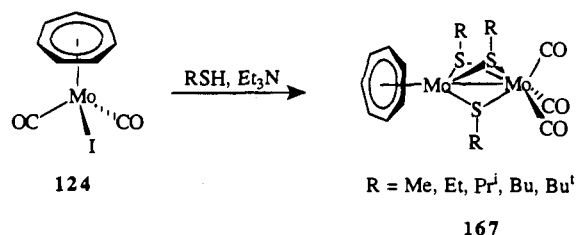
Scheme 66



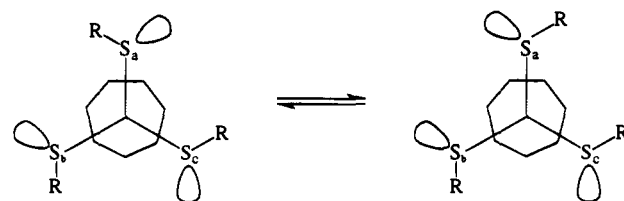
Scheme 67



Scheme 68



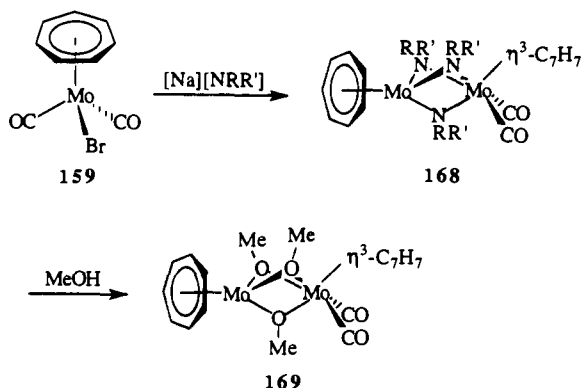
Scheme 69



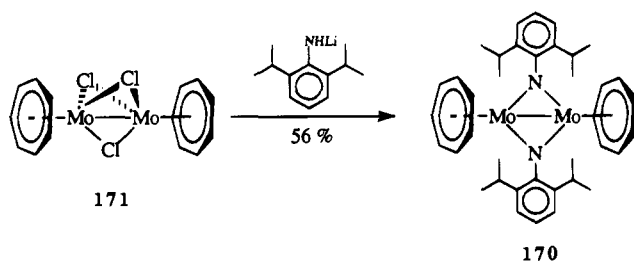
treatment with dppe, is converted into the cation **165**. Further reaction with $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ in refluxing acetonitrile leads to CO substitution forming the complex **166** (Scheme 67).¹³⁵

Treatment of **124** with thiols RSH (R = Me, Et, Prⁱ, Bu, or Bu^t) in the presence of triethylamine produces a series of unsymmetric thiolato-bridged complexes $\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\mu\text{-SR})_3\text{Mo}(\text{CO})_3$ (**167**) (Scheme 68).^{142,143} Infrared and variable-temperature NMR spectroscopy reveal that the complexes exist as two isomers differing in the relative orientations of the R groups on bridging sulfur (Scheme 69). These isomers interconvert rapidly at ambient temperature, attributed to a low-energy sulfur inversion process.¹⁴³ The monosubstituted derivatives $\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\mu\text{-SBu}^t)_3\text{Mo}(\text{CO})_2\text{L}$ [L = P(OMe)₃, PMePh₂, PMe₂Ph, or PMe₃], prepared from the reaction of **167** (R = Bu^t) and the corresponding phosphorus donors, also exhibit such fluxional process and the free energies of activation for sulfur inversion have been estimated ranging from 46.7 to 58.8 kJ/mol. The selenium analogs of **167** have also been prepared similarly.¹⁴²

Scheme 70



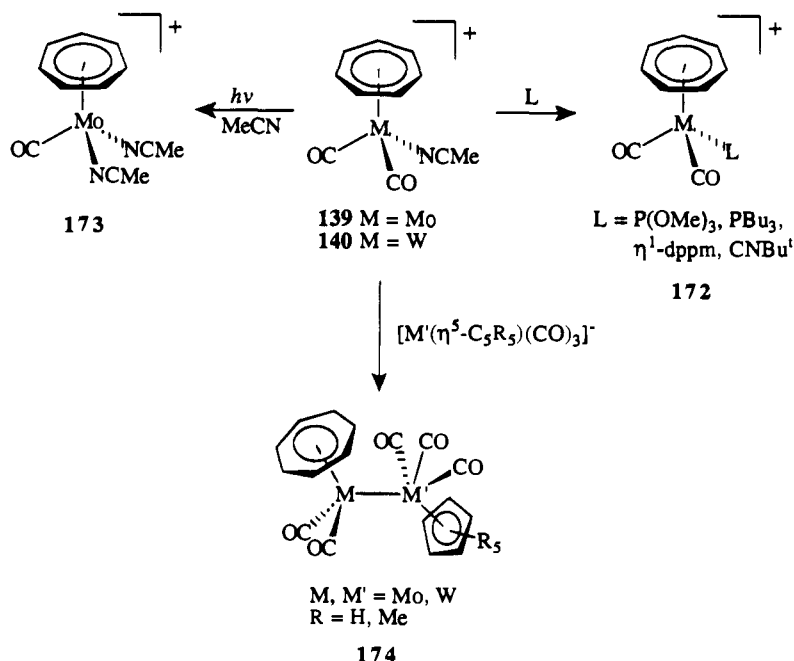
Scheme 71



and the X-ray structure of $\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\mu\text{-SePh})_3\text{Mo}(\text{CO})_3$ has been determined.¹⁴⁴

The triply amido-bridged molybdenum compounds $\text{Mo}(\eta^3\text{-C}_7\text{H}_7)(\text{CO})_2(\mu\text{-NRR}')_3\text{Mo}(\eta^7\text{-C}_7\text{H}_7)$ ($\text{NRR}' = \text{NH}_2$, NC_4H_4 , NHPH , or $\text{NHC}_6\text{H}_4\text{NO}_2$) (**168**) can be synthesized, in low yields, by treating $\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{CO})_2\text{Br}$ (**159**) with the corresponding amides. For $\text{NRR}' = \text{NH}_2$, it is much more convenient to prepare from $\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{CO})_2\text{Me}$ in liquid ammonia. These amido compounds react with MeOH forming the bridging methoxy compounds **169** (Scheme 70).¹⁴⁵ The related bridging-imido complex **170** has recently been reported.¹⁴⁶ The synthesis involves treatment of **171** with ArNHLi (Scheme 71).

Scheme 72

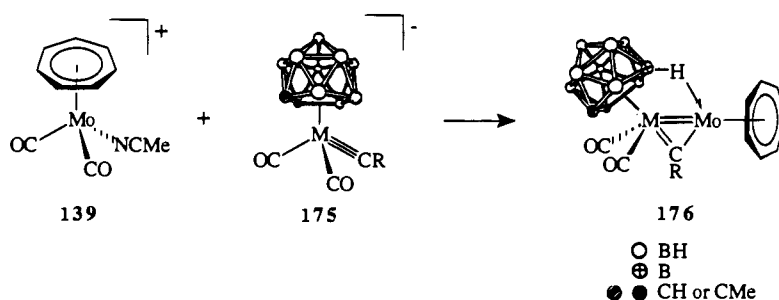


Whiteley *et al.* have demonstrated that the cations **139** and **140** are useful precursors to other cycloheptatrienyl derivatives of molybdenum and tungsten. As shown in Scheme 72, the acetonitrile ligand of these cations is labile and can be displaced readily by various donors, such as PR_3 ($\text{R} = \text{OMe}$ or Bu), dppm , and CNBu^t , forming the monosubstituted products **172**.^{108,128} Photolysis of the molybdenum complex **139** in acetonitrile leads to CO substitution giving the bisacetonitrile cation **173**.^{108,127} A series of metal-metal-bonded complexes $\text{M}(\eta^7\text{-C}_7\text{H}_7)(\text{CO})_2\text{M}'(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_3$ ($\text{M}, \text{M}' = \text{Mo}$ or W ; $\text{R} = \text{H}$ or Me) (**174**) have also been prepared from **139** and **140** and the appropriate anions $[\text{M}'(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_3]^-$.^{127,147} The molecular structure of **174** ($\text{M} = \text{M}' = \text{Mo}$; $\text{R} = \text{H}$) shows an unsupported metal-metal bond and a *trans* arrangement of the C_5 and C_7 rings.¹⁴⁸

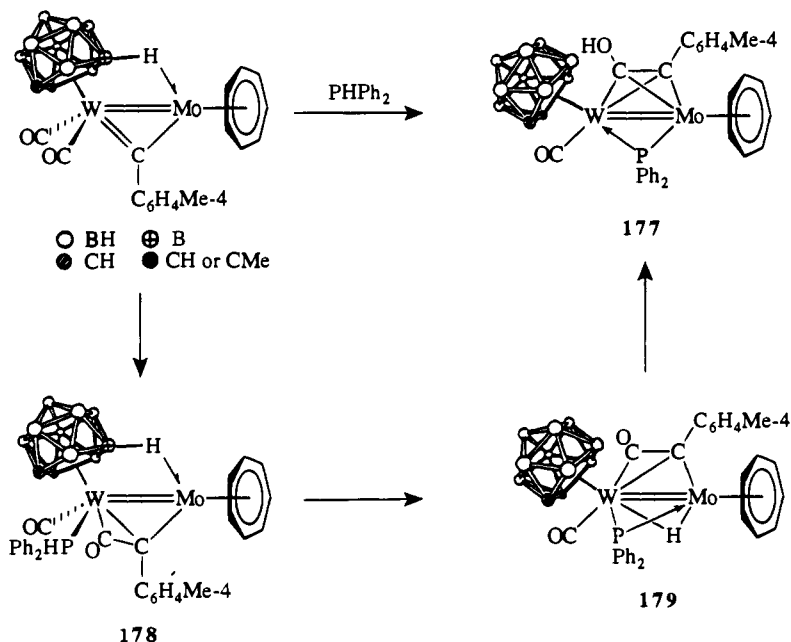
The molybdenum complex **139** has also been employed by Stone *et al.* to react with the carborane metal carbynes **175**.¹⁴⁹ The reactions give the bimetallic complexes $\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\mu\text{-CR})\text{M}(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{R}^1\text{R}^2)(\text{CO})_2$ ($\text{M} = \text{Mo}$ or W ; $\text{R} = \text{C}_6\text{H}_4\text{Me-4}$, $\text{C}_6\text{H}_4\text{Me-2}$, or $\text{C}\equiv\text{CBu}^t$; $\text{R}^1, \text{R}^2 = \text{H}$ or Me) (**176**), which have a metal-metal bond bridged by an alkylidyne group and a $\text{B-H}\rightarrow\text{Mo}$ agostic bond (Scheme 73). The related complex $\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\mu\text{-CC}_6\text{H}_4\text{Me-4})\text{W}(\eta^6\text{-C}_2\text{B}_{10}\text{H}_{10}\text{Me}_2)(\text{CO})_2$ has also been synthesized from **139** and $[\text{Net}_4][\text{W}(\eta^6\text{-C}_2\text{B}_{10}\text{H}_{10}\text{Me}_2)(\text{CO})_2(\equiv\text{CC}_6\text{H}_4\text{Me-4})]$.

While treatment of **176** ($\text{M} = \text{W}$; $\text{R} = \text{C}_6\text{H}_4\text{Me-4}$; $\text{R}^1 = \text{R}^2 = \text{Me}$) with PMe_3 displaces one of the CO ligands,¹⁴⁹ the reaction of **176** ($\text{M} = \text{W}$; $\text{R} = \text{C}_6\text{H}_4\text{Me-4}$; $\text{R}^1 = \text{H}$; $\text{R}^2 = \text{H}$ or Me) and PPh_2 produces the complexes **177**, which have an unusual structure established by X-ray crystallography (Scheme 74).¹⁵⁰ Presumably, addition of PPh_2 leads to attack of CO on the μ -alkylidyne fragment, giving the intermediate **178**. A metal-assisted hydrogen transfer from the coordinated PPh_2 molecule to the ketenyl oxygen atom, accompanied with migration of the resulting

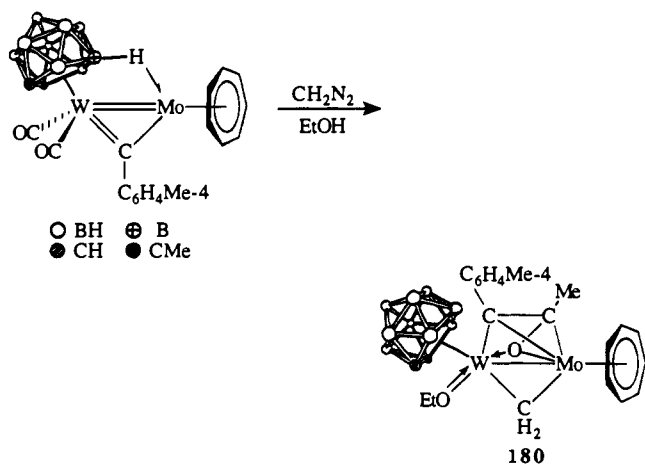
Scheme 73



Scheme 74



Scheme 75



phosphido ligand into the bridging position via intermediate **179**, could lead to the product **177**.

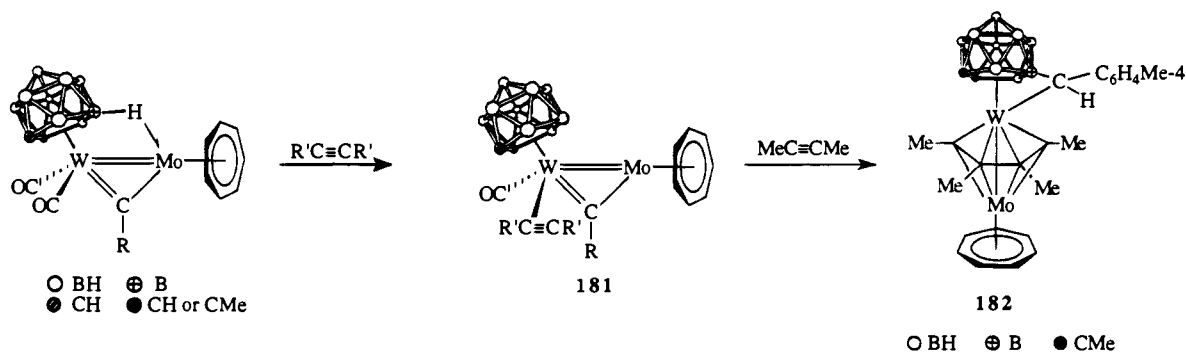
The complex **176** ($M = W$; $R = C_6H_4Me-4$; $R^1 = H$; $R^2 = Me$) also reacts with diazomethane in ether containing ethanol to give the methylene bridged complex **180**, of which the structure has been determined and the plausible mechanism of formation has been proposed (Scheme 75).¹⁵¹

The reaction of **176** and alkynes has also been studied.¹⁵² The complexes **176** ($M = W$; $R = C_6H_4Me-4$ or $C \equiv CMe$; $R^1 = Me$; $R^2 = H$ or Me) react with

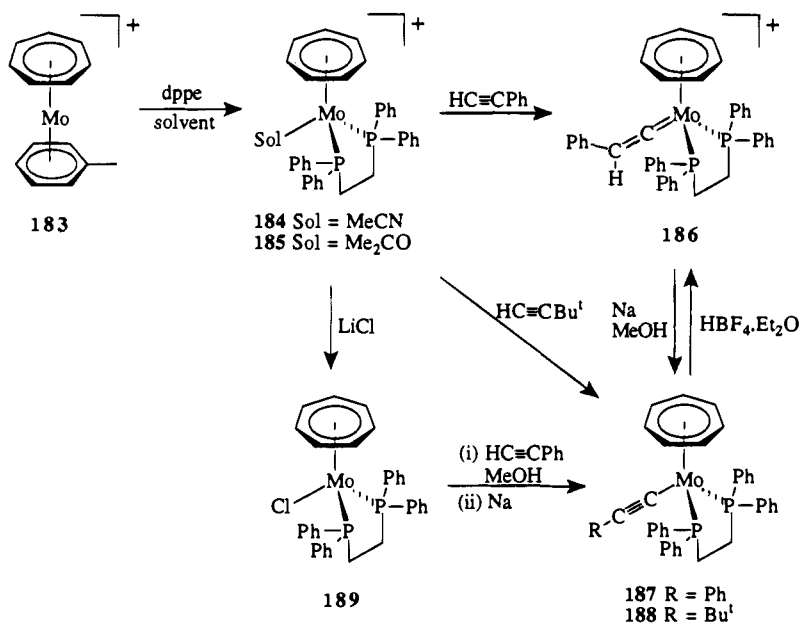
$R'C \equiv CR'$ ($R' = Me, Et, \text{ or } Ph$) to give the substituted products **181** in which the agostic bond is absent. Treatment of **181** ($R = C_6H_4Me-4$; $R' = Me$) with $MeC \equiv CMe$ at higher temperature ($100^\circ C$) leads to the novel compound **182** (Scheme 76). The X-ray crystal structure shows that the $Mo-W$ bond is symmetrically bridged by a $\mu-\eta^4-C_4Me_4$ fragment and the tungsten atom is ligated by a $CH(C_6H_4Me-4)-C_2B_9H_8Me_2$ moiety.

The mixed-sandwich cation $[Mo(\eta^7-C_7H_7)(\eta^6-C_6H_5Me)]^+$ (**183**), which can be prepared by either treating $[Mo(\eta^6-C_6H_5Me)(\eta^3-C_3H_5)Cl]_2$ with $(AlEtCl_2)_2$ in the presence of cycloheptatriene¹⁵³ or refluxing $[Mo(\eta^7-C_7H_7)(CO)_3]^+$ (**98**) in toluene,¹⁵⁴ is an excellent precursor to cycloheptatrienyl molybdenum derivatives.¹⁵⁴⁻¹⁵⁷ Recently, the synthetic utility of this compound has been extended. For example, treatment of **183** with 1 equiv of *dppe* in acetonitrile or acetone causes displacement of the toluene ligand giving $[Mo(\eta^7-C_7H_7)(dppe)(solvent)]^+$ [*solvent* = $MeCN$ (**184**) or acetone (**185**)].¹⁵⁷ These complexes react with $HC \equiv CPh$ forming the phenylvinylidene complex **186**, which is readily deprotonated to give the alkynyl complex **187**. By contrast, the reaction of **185** with $HC \equiv CMe$ affords the corresponding alkynyl complex **188** directly. Alternatively, the compound $Mo(\eta^7-C_7H_7)(dppe)Cl$ (**189**), which is readily available from **185** and $LiCl$, reacts with $HC \equiv CPh$ in refluxing methanol followed by the addition of sodium, giving

Scheme 76



Scheme 77

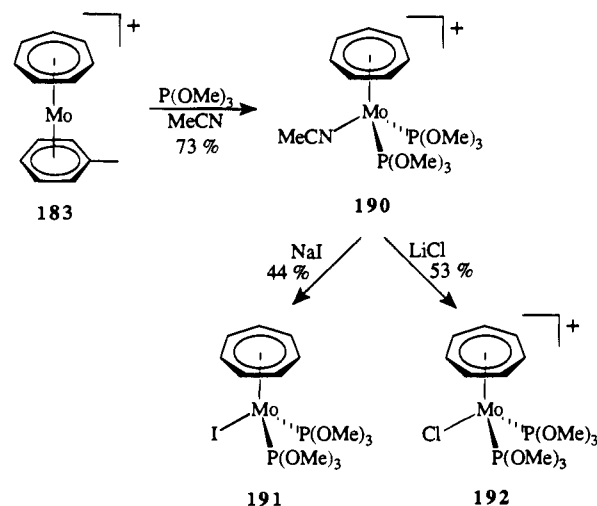


187 in moderate yield. Upon protonation with HBF₄·Et₂O, compound **187** regenerates **186** (Scheme 77).¹⁵⁸ Similarly, the compound Mo(η⁷-C₇H₇)(CO)(PMe₃)(C≡CPh) can also be protonated to give the carbene [Mo(η⁷-C₇H₇)(CO)(PMe₃)(C=CHPh)]⁺ in 64% yield.¹³⁶ The analogous dicarbonylalkynyl complexes M(η⁷-C₇H₇)(CO)₂(C≡CPh) (M = Mo or W) have also been prepared by treating Mo(η⁷-C₇H₇)(CO)₂I (**124**) or W(η⁷-C₇H₇)(CO)₂Cl (**125**) with LiC≡CPh.^{158b}

Heating **183** in acetonitrile with 2 equiv of P(OMe)₃, instead of **1** equiv of dppe, affords the related cation {Mo(η⁷-C₇H₇)[P(OMe)₃]₂(MeCN)}⁺ (**190**). This reacts with NaI giving the neutral compound **191**. However, reaction with LiCl produces the paramagnetic cation **192** (Scheme 78).¹³⁵

The reaction of **183** with thiols has also been studied.¹⁵⁹ The reactions give a new series of binuclear thiolato-bridged molybdenum complexes [Mo₂(η⁷-C₇H₇)₂(μ-SR)₃]⁺ (R = Pr, Bu, Ph, or CH₂Ph) (**193**). The thioethoxyl analog [Mo₂(η⁷-C₇H₇)₂(μ-SEt)₃]⁺ has also been prepared by treating **183** with LiSEt. An alternative route to these binuclear compounds is through the paramagnetic cation [Mo(η⁷-C₇H₇)(η⁵-C₇H₉)]⁺ (**7**). Treatment of **7** with benzenethiol or phenylmethanethiol gives **193** (R = Ph or CH₂Ph) in good yields (Scheme 79). Dynamic NMR studies reveal that all of these complexes (except for R = Ph) are fluxional due to the inversion at the pyramidal

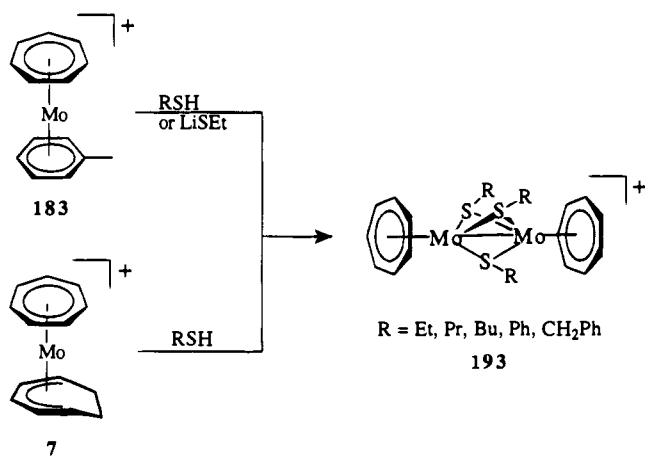
Scheme 78



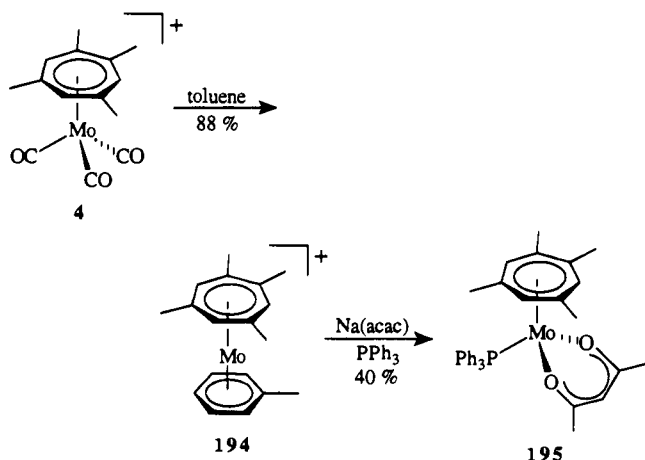
sulfur center. The activation free energies of this process range from 52.9 to 58.1 kJ/mol and increase in the order R = CH₂Ph < Bu < Pr < Et.

The tetramethyl-substituted analog of **183**, namely [Mo(η⁷-C₇H₃Me₄-1,2,4,6)(η⁶-C₆H₅Me)]⁺ (**194**), which can be prepared by refluxing [Mo(η⁷-C₇H₃Me₄-1,2,4,6)-(CO)₃]⁺ (**4**) in toluene, shows diminished reactivity in comparison with **183**. Nevertheless, it reacts with benzenethiol producing the binuclear cation [Mo₂(η⁷-

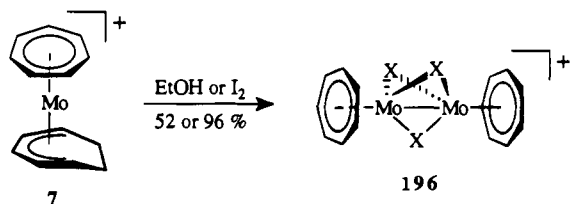
Scheme 79



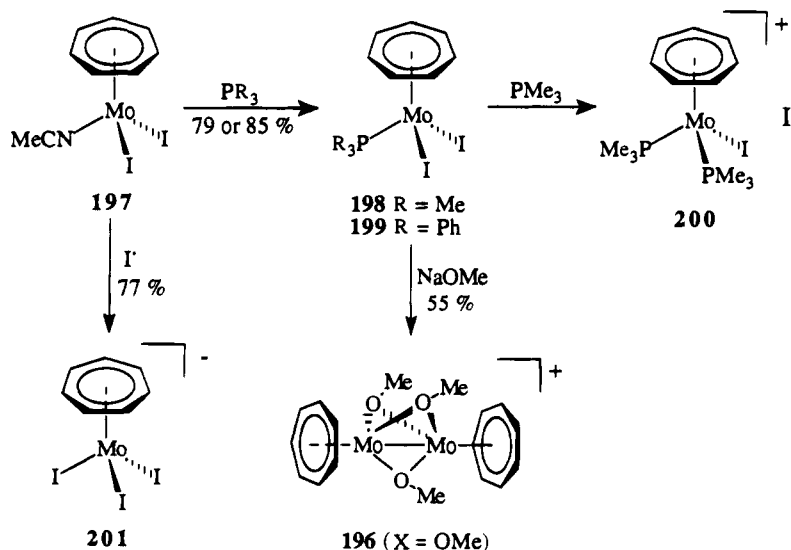
Scheme 80



Scheme 81



Scheme 82



$\text{C}_7\text{H}_3\text{Me}_4\text{-1,2,4,6)}_2(\mu\text{-SPh})_3]^+$ in excellent yield.¹⁵⁹ Upon treatment with sodium acetylacetonate $[\text{Na}(\text{acac})]$ and PPh_3 , it converts into compound **195** (Scheme 80).¹²

The cation $[\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_7\text{H}_9)]^+$ (**7**) also reacts with ethanol or iodine forming the dimeric species $[\text{Mo}_2(\eta^7\text{-C}_7\text{H}_7)_2(\mu\text{-X})_3]^+$ (X = OEt or I) (**196**) (Scheme 81).⁴¹ These reactions, together with the reaction with thiols,¹⁵⁹ show the ease with which nucleophiles react with **7** to displace the $\eta^5\text{-C}_7\text{H}_9$ group. Indeed, solutions of this compound in halogenated solvents are unstable and decompose slowly.

The 17-electron compound $\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{MeCN})\text{I}_2$ (**197**) undergoes ligand substitution reaction with PR_3 (R = Me or Ph) giving $\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{PR}_3)\text{I}_2$ [R = Me (**198**) or Ph (**199**)]. The former complex, upon further reaction with PMe_3 , yields the salt $[\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{PMe}_3)_2\text{I}][\text{I}]$ (**200**), whereas reaction with NaOMe produces **196** (X = OMe).⁴¹ The acetonitrile ligand of **197** can also be displaced by weak anionic nucleophiles, such as iodide ion. Thus treatment of **197** with 1 equiv of $[\text{Bu}_4\text{N}][\text{I}]$ gives $[\text{Bu}_4\text{N}][\text{Mo}(\eta^7\text{-C}_7\text{H}_7)\text{I}_3]$ (**201**) of which the structure confirms a three-legged piano stool structure (Scheme 82).^{41b} Displacement of acetonitrile ligand in analogous $\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{MeCN})\text{Br}_2$ ⁴¹ and $\text{W}(\eta^7\text{-C}_7\text{H}_7)(\text{MeCN})\text{I}_2$ ⁴² with Et_2S and PMe_3 occurs readily producing the complexes $\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{Et}_2\text{S})\text{Br}_2$ and $\text{W}(\eta^7\text{-C}_7\text{H}_7)(\text{PMe}_3)\text{I}_2$, respectively.

5. Redox Reactions

Sandwich compounds almost invariably undergo electron-transfer reactions and the electrochemistry of this class of compounds has been studied extensively. Table 1 summarizes the electrochemical data of $\text{M}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_5\text{H}_5)$ and their derivatives, obtained by cyclic voltammetry, as well as the gas-phase first vertical ionization potentials (IP) obtained by photoelectron spectroscopy. It is worth noting that, for the group 4 compounds, the influence of metal changes upon the ionization energies of the HOMO e_2 is evidently small.¹⁶¹ However, the transition $e_2 \rightarrow a_1$, according to the UV-vis electronic absorption spectra, shifts to higher energy along the

Table 1. Electrochemical Data of Sandwich Compounds $M(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_5\text{R}_5)$ and Derivatives

compound	$E_{1/2}(0/+1)$ (V) ^a	$E_{1/2}(0/-1)$ (V) ^a	IP (eV) ^b	ref(s)
Ti($\eta^7\text{-C}_7\text{H}_7$)($\eta^5\text{-C}_5\text{H}_5$)	+0.15 ^c	-2.07 ^c	6.86, 6.95, 6.83	160-162, 59
Ti($\eta^7\text{-C}_7\text{H}_7$)($\eta^5\text{-C}_5\text{H}_4\text{Me}$)			6.82	161
Ti($\eta^7\text{-C}_7\text{H}_7$)($\eta^5\text{-C}_5\text{Me}_5$)	+0.13 ^c	-2.14 ^c	6.70	160, 161
Zr($\eta^7\text{-C}_7\text{H}_7$)($\eta^5\text{-C}_5\text{H}_5$)			6.94	162
Zr($\eta^7\text{-C}_7\text{H}_7$)($\eta^5\text{-C}_5\text{Me}_5$)			6.72	161
Hf($\eta^7\text{-C}_7\text{H}_7$)($\eta^5\text{-C}_5\text{Me}_5$)			6.67	161
V($\eta^7\text{-C}_7\text{H}_7$)($\eta^5\text{-C}_5\text{H}_5$)	+0.19, ^c +0.26 ^d	-2.55 ^d	6.49, 6.42	37, 163, 59
Nb($\eta^7\text{-C}_7\text{H}_7$)($\eta^5\text{-C}_5\text{H}_5$)	-0.82 ^c	-2.40 ^{e,f}	5.85, 5.98	37, 48b, 162
Nb($\eta^7\text{-C}_7\text{H}_7$)($\eta^5\text{-C}_5\text{H}_4\text{Me}$)	-0.82 ^c	-2.40 ^{e,f}		37, 48b
Ta($\eta^7\text{-C}_7\text{H}_7$)($\eta^5\text{-C}_5\text{H}_4\text{Me}$)	-1.18 ^c		5.47	37
Cr($\eta^7\text{-C}_7\text{H}_7$)($\eta^5\text{-C}_5\text{H}_5$)	-0.61 ^c	-2.89 ^{d,g}	5.59	163, 59
Mo($\eta^7\text{-C}_7\text{H}_7$)($\eta^5\text{-C}_5\text{H}_5$)	-0.60 ^c		5.87, 5.70	41b, 162, 60
Mo($\eta^7\text{-C}_7\text{H}_7$)($\eta^5\text{-C}_5\text{H}_4\text{Me}$)	-0.63 ^c			41b
Mo($\eta^7\text{-C}_7\text{H}_7$)($\eta^5\text{-C}_9\text{H}_7$)	-0.48 ^c			41b
W($\eta^7\text{-C}_7\text{H}_7$)($\eta^5\text{-C}_5\text{H}_5$)	-0.77 ^c		5.58	42b, 164
W($\eta^7\text{-C}_7\text{H}_7$)($\eta^5\text{-C}_5\text{H}_4\text{Me}$)	-0.79 ^c		5.50	42b, 164
W($\eta^7\text{-C}_7\text{H}_7$)($\eta^5\text{-C}_9\text{H}_7$)	-0.66 ^c			42b

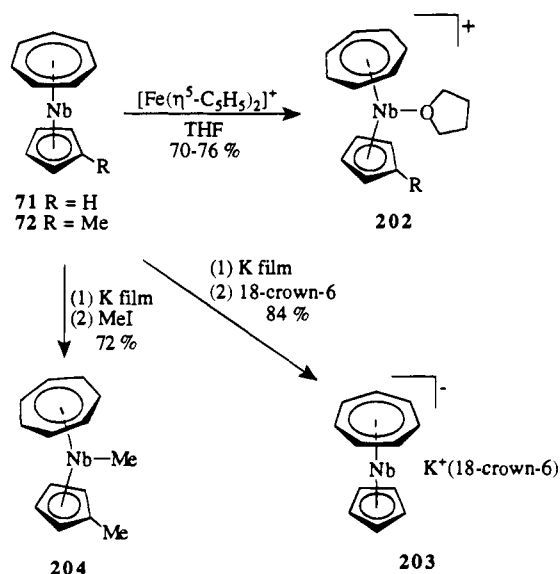
^a Half-wave potentials vs SCE; waves are reversible unless stated otherwise. ^b Gas-phase ionization potentials. ^c In MeCN. ^d In dme. ^e In THF. ^f Quasi-reversible. ^g Irreversible.

group which must be attributed to an increase in energy of the LUMO a_1 .^{32,161} A similar trend is not observed for the group 5 and 6 metal complexes.

The electrochemically generated $[\text{Ti}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_5\text{H}_5)]^-$ species has been characterized by EPR.¹⁶⁵ The room temperature spectrum shows an unpaired electron spin $S = 1/2$ interacting with proton nuclei of the C_5 and C_7 rings. The coupling due to ^{47}Ti and ^{49}Ti is also partially resolved. By deuterating the cyclopentadienyl ligand, the EPR spectrum is significantly simplified and from these spectra, magnetic parameters can be determined as $g_{\text{iso}} = 1.986(9)$, $A_{\text{iso}}(\text{C}_5) = +4$ MHz, $A_{\text{iso}}(\text{C}_7) = +13$ MHz, and $A_{\text{iso}}(\text{Ti}) = 24$ MHz. The structure of the radical anion has also been determined by proton ENDOR at low temperature which shows that the geometry of the parent neutral molecule is preserved upon this one-electron reduction.¹⁶⁵

Chemical oxidation and reduction of $\text{Nb}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_5\text{H}_4\text{R})$ [$\text{R} = \text{H}$ (**71**) or Me (**72**)] have been reported.^{37,48b} Treatment of these compounds with 1 equiv of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]^+$ in THF gives the cations **202**, in which the THF ligand can be displaced with CO and PMe_3 . The X-ray structure of **202** ($\text{R} = \text{Me}$) (Figure 3) confirms a bent sandwich structure with a coordinated THF ligand. In contrast, the 16-electron vanadium analog $[\text{V}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_5\text{H}_5)]^+$ shows no tendency to form stable 18-electron adducts,¹⁶⁶ presumably because of the smaller atomic radius of vanadium. Reduction of **71** with a freshly prepared potassium film followed by the addition of 18-crown-6 affords the crystallographically characterized salt **203**. Similar treatment of **72** gives the corresponding anion which reacts with MeI to produce **204** in good yield (Scheme 83).³⁷

The electrochemistry of $M(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_5\text{H}_5)$ ($M = \text{V}$ or Cr) has been examined and compared with the dibenzene analogs.¹⁶³ It has been shown that oxidation of the chromium species is easier than that of the vanadium counterparts and the symmetrical dibenzene complexes are oxidized preferentially to the mixed-ring analogs. Presumably, in the case of chromium complexes, an electron is removed from the doubly occupied HOMO a_1 , thereby decreasing Coulomb repulsion, whereas for the vanadium complexes

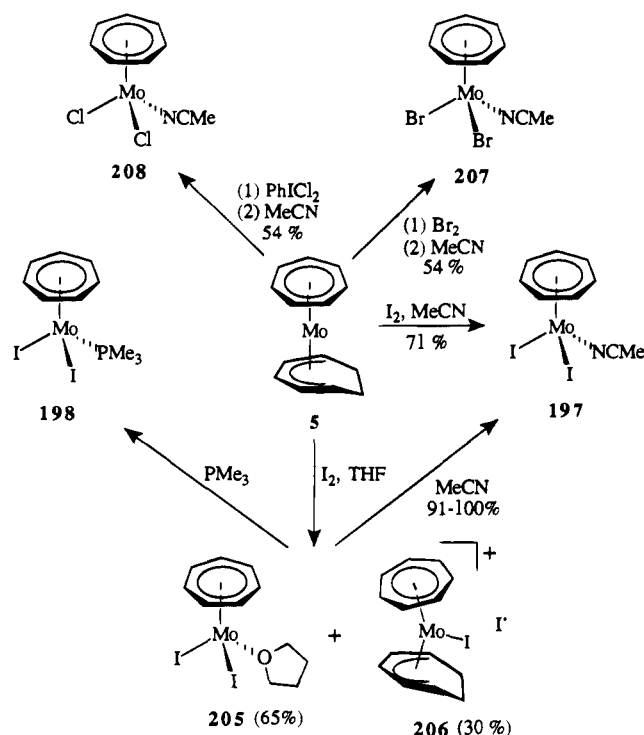
Scheme 83

this HOMO is singly occupied and the electron is bound more tightly. The latter observation is a consequence of the higher electron-accepting properties of the ligand combination $\text{C}_5 + \text{C}_7$ ring compared to $\text{C}_6 + \text{C}_6$ ring. A linear correlation between the ionization potential (IP) and half-wave potential ($E_{1/2}$) has also been established and can be represented by the equation $\text{IP} = 0.99E_{1/2} + 6.20$ eV.

The vapor-phase UV-vis absorption spectrum of $\text{Cr}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_5\text{H}_5)$ has been measured which shows surprisingly well-resolved Rydberg structure. The three Rydberg series converge to the same ionization limit 5.603 ± 0.007 eV, which is in good agreement with the values obtained by photoelectron spectroscopy.¹⁶⁷

The sandwich compounds $M(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_5\text{H}_5)$ ($M = \text{Mo}$ or W) can be oxidized with iodine to give the corresponding cations.¹⁶⁸ Recently, several interesting charge-transfer complexes and intercalation compounds have been prepared by these species and their derivatives. Treatment of $\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_5\text{H}_4\text{Me})$ with a stoichiometric amount of TCNE results in the formation of $[\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_5\text{H}_4\text{Me})][\text{TCNE}]$.^{41b} The

Scheme 84

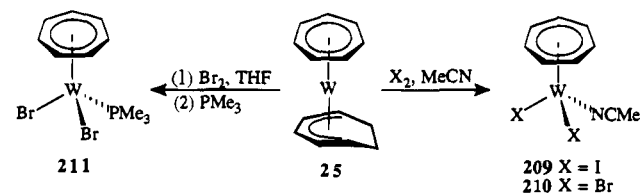


IR, EPR, and magnetic susceptibility measurements reveal that the solid state structure of the salt consists of the diamagnetic dimeric dianion $[\text{TCNE}]_2^{2-}$. Similar reaction of $\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_5\text{H}_5)$ and TCNQ gives the 2:1 charge-transfer salt $[\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_5\text{H}_5)]_2[\text{TCNQ}]$. Intercalation of $\text{M}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_5\text{H}_4\text{-Me})$ ($\text{M} = \text{Mo}$ or W) into layered ZrS_2 leads to the intercalates $\{\text{ZrS}_2[\text{M}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_5\text{H}_4\text{Me})]_x\}$ [$x = 0.22$ (Mo) or 0.20 (W)] of which the lattice expansion has been determined by X-ray powder diffraction.^{42b}

Compound $\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_7\text{H}_9)$ (**5**) undergoes a reversible one-electron oxidation at $E_{1/2} = -0.19$ V relative to the ferrocenium-ferrocene couple (or $+0.17$ vs SCE) as shown by cyclic voltammetry.²¹ Chemical oxidation of **5** to the monocation $[\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_7\text{H}_9)]^+$ (**7**) can be achieved by the action of 1 equiv of AgBF_4 , excess amount of HBF_4 or 0.5 equiv of I_2 . Reduction of **7** back to the corresponding neutral molecule can be effected with 1% sodium amalgam.^{21,41} Treatment of **5** with 1 equiv of iodine in THF, however, gives a mixture of **205** and **206**. The air-stable, but thermally-unstable, compound **205** has been crystallographically characterized,¹⁶⁹ while the structure of **206** has only been tentatively assigned on the basis of its spectroscopic data. Both of these compounds react with MeCN and PMe_3 giving **197** and **198**, respectively. An improved route to **197** is the oxidation of **5** with iodine in MeCN from which the air- and thermally-stable **197** can be isolated in 71% yield. Similarly, oxidation of **5** with Br_2 or PhICl_2 in THF or toluene, followed by the addition of MeCN results in the formation of **207** or **208**, respectively (Scheme 84).^{41,170}

These synthetic routes can be extended to tungsten.^{42,170} Thus, treatment of $\text{W}(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_7\text{H}_9)$ (**25**) with 1 equiv of I_2 in MeCN gives **209** in excellent yield. By using Br_2 as oxidant, only a small amount of **210** is obtained. However, reaction of **25** with 1

Scheme 85



equiv of Br_2 in THF followed by the treatment of PMe_3 leads to the isolation of **211** in moderate yield (Scheme 85).

It is worth mentioning that the 17-electron complexes $\text{M}(\eta^7\text{-C}_7\text{H}_7)\text{LX}_2$ ($\text{M} = \text{Mo}$ or W ; $\text{L} = \text{MeCN}$ or PMe_3 ; $\text{X} = \text{Br}$ or I) exhibit antiferromagnetic interactions with temperatures at χ_{max} ranging from 12 to 17 K. The magnetic susceptibility data can be described by one-dimensional magnetic models and this is supported by the crystal structure of $\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{MeCN})\text{I}_2$ (**197**) which, as shown in Figure 11, reveals the structure to consist of chains of molecules. The shortest intermolecular distance within a chain is 3.670 Å and occurs between I(1) and C(5) of the C_7 ring. This distance is shorter than the sum of the van der Waals radii of carbon and iodine (4.00 Å). The neighboring chains are arranged antiparallel to each other as shown in Figure 11, parts a and d. The distance between the centroids of C_7 rings of adjacent molecules is 3.710 Å, which is close to the interlayer distance of graphite (3.35 Å). Figure 12 shows the temperature variation of magnetic susceptibility for **197**. The maximum at 16 K and the negative Weiss constant (-5.2 K) derived at higher temperature (50–300 K) provide strong evidence for antiferromagnetic interactions. The solid line, which is the theoretical curve based on an one-dimensional Heisenberg model, closely corresponds to the experimental data and from which the values of g (1.84) and exchange constant J (-8.9 K) can be calculated. By similar analyses, the J values for other compounds can also be obtained. Interestingly, some general trends can be observed from these data. Firstly, changing the metal center from Mo to W increases the exchange constant by 1.2–1.9 K, which may be attributed to the fact that the d electrons in W are more diffuse than those in Mo, thus the interaction along the chain between W–W would be stronger than for Mo–Mo. Secondly, changing the ligand from MeCN to PMe_3 decreases the J value by 2.0–3.7 K. It is likely that the more bulky PMe_3 ligand would lengthen the metal–metal separation in the chain resulting in smaller values for J . Finally, changing the halogen from iodine to bromine also decreases the value of J by 0.4–0.7 K. It is noteworthy that the chloro analog $\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{MeCN})\text{Cl}_2$ (**208**) does not show antiferromagnetic coupling. These may suggest that the efficiency of super-exchange pathway via M-X-M follows the order $\text{X} = \text{I} > \text{Br} > \text{Cl}$.

Reduction of **197** with 1 equiv of Na/Hg in the presence of 2 equiv of PMe_3 or 1 equiv of dmpe or dppe results in the formation of diamagnetic $\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{L})\text{I}$ [$\text{L} = (\text{PMe}_3)_2$ (**212**), dmpe (**213**), or dppe (**214**)] (Scheme 86).⁴¹ Similarly, treatment of the tungsten complex $\text{W}(\eta^7\text{-C}_7\text{H}_7)(\text{MeCN})\text{I}_2$ (**209**) with Na/Hg in the presence of dmpe gives $\text{W}(\eta^7\text{-C}_7\text{H}_7)(\text{dmpe})\text{I}$.⁴² The compounds **197**, **209**, and **211** also

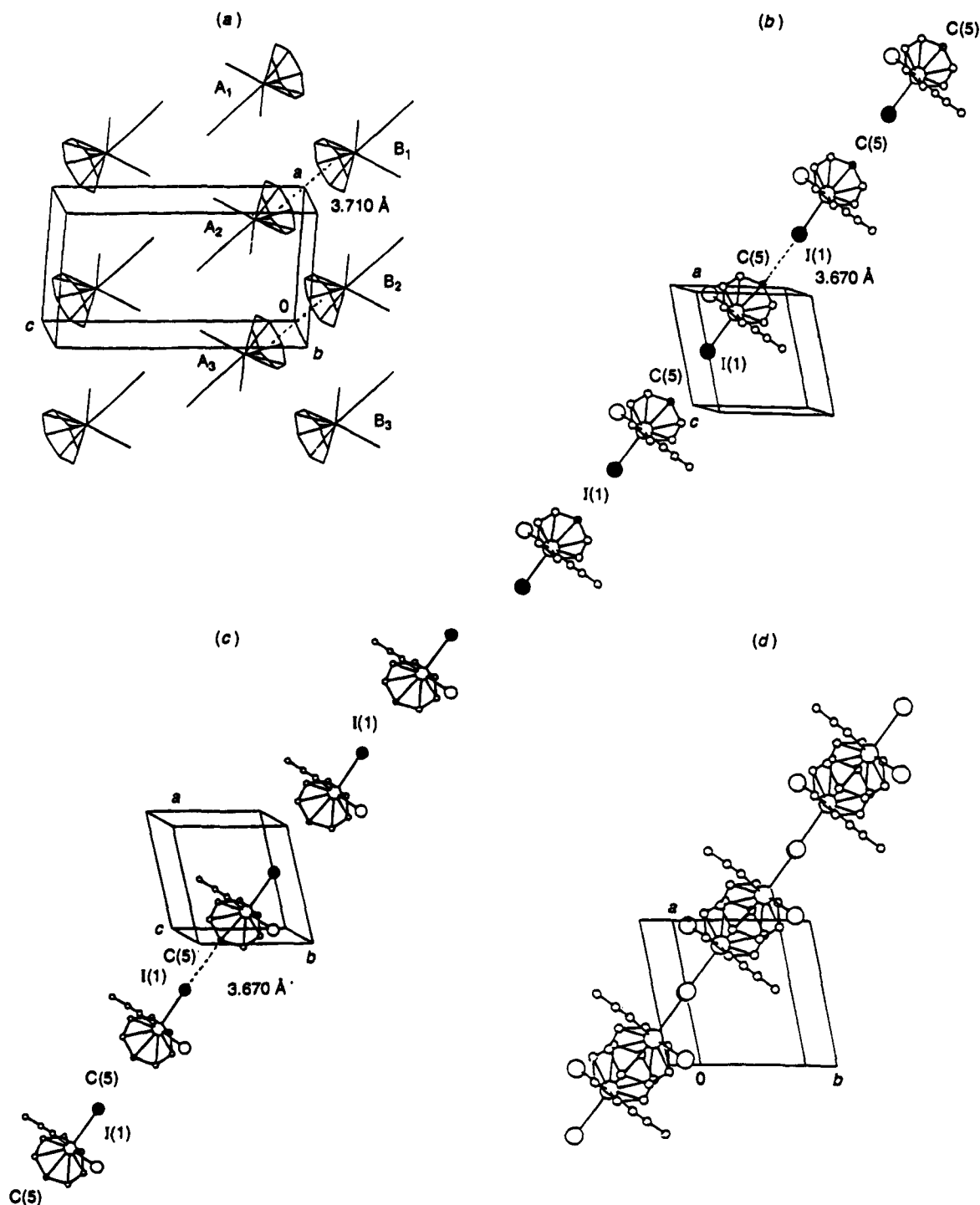


Figure 11. Crystal structure of $\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{MeCN})\text{I}_2$: (a) view along the b axis, (b) view of molecules A_x along the c axis, (c) view of molecules B_x along the c axis, (d) view along the c axis.

react with an excess of NaC_5H_5 , $\text{NaC}_5\text{H}_4\text{Me}$, or LiC_9H_7 giving the corresponding mixed-sandwich compounds (Scheme 87).^{41,42}

The electrochemical reduction of tropylium cation, $[\text{M}(\eta^7\text{-C}_7\text{H}_7)(\text{CO})_3]^+$ [$\text{M} = \text{Cr}$ (**97**), Mo (**98**), or W (**94**)], and $[\text{Cr}(\eta^7\text{-C}_7\text{H}_6\text{R})(\text{CO})_3]^+$ ($\text{R} = \text{Me}$, Et , Pr^i , or Bu^t) has been investigated.^{171,172} The free cation undergoes a one-electron reduction leading to the neutral radical $[\text{C}_7\text{H}_7]^\cdot$, which immediately dimerizes. In contrast, the complexed cations are reduced through a 2-electron reversible step to the corresponding anions $[\text{M}(\eta^7\text{-C}_7\text{H}_6\text{R})(\text{CO})_3]^-$, which, in the absence of proton source, couple with the parent cations, pro-

ducing the dimer $[\text{M}(\text{CO})_3]_2(\eta^6:\eta^6\text{-C}_{14}\text{H}_{12}\text{R}_2)$. The rate of dimerization is strongly affected by the size of the alkyl group. In MeCN and acetic acid mixture, the anions undergo a competitive attack from protons and cations, and the ratio of the resulting products depends on both the alkyl substituent and the nature of metal. Chemical reduction of **97** and **98** to form the dimer can be achieved with chromium(II) prepared in situ from $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and zinc.¹⁷³ Reaction of **97**, **98**, and **94** with carbonylmetalates $[\text{W}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]^-$ or $[\text{Mn}(\text{CO})_5]^-$ does not lead to nucleophilic attack on the C_7 ring. Instead, it gives the corresponding dimers $[\text{M}(\text{CO})_3]_2(\eta^6:\eta^6\text{-C}_{14}\text{H}_{14})$ in mod-

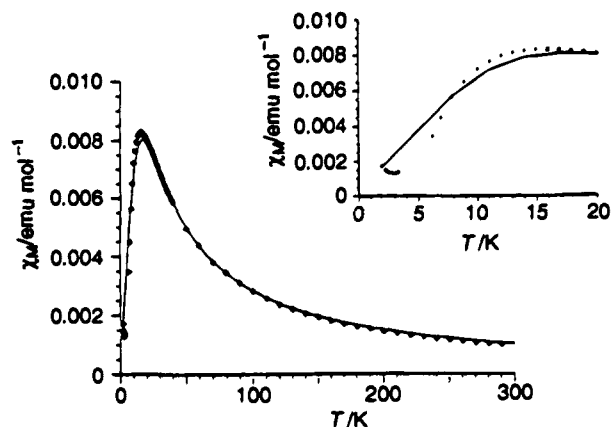
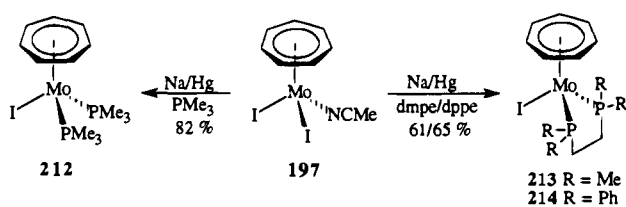
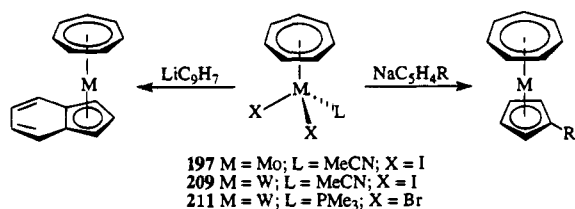


Figure 12. Magnetic susceptibility data for $\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{MeCN})\text{I}_2$ at 1 T. The solid line is the best fit based on the one-dimensional Heisenberg model. The inset shows an expansion of the low-temperature region.

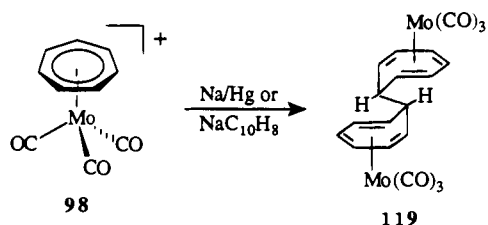
Scheme 86



Scheme 87



Scheme 88



erate yield.¹⁷⁴ Treatment of **98** with either sodium amalgam or sodium naphthalide also leads to reductive dimerization to the ditropyl complex **119**. The X-ray structure of the product confirms that the hydrogen atoms attached to the bridging carbon atoms are both *endo* as shown in Scheme 88.¹⁷⁵

Recently, the redox behavior of $\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{CO})_2(\sigma\text{-C}_6\text{F}_5)$ (**215**) has been examined. It displays a reversible 1 electron oxidation at +0.49 V vs Fc^+/Fc . Chemical oxidation in methanol, however, leads to partial CO insertion giving *ca.* 50% yield of $\text{C}_6\text{F}_5\text{CO}_2\text{-Me}$ and $\text{C}_6\text{F}_5\text{H}$.¹⁷⁶ The compound **215** can be reduced either chemically or electrochemically by one electron ($E_{\text{pc}} = -2.07$ V vs Fc^+/Fc) forming the bicycloheptatrienyl dianion **216**.¹⁷⁷ In the presence of $\text{P}(\text{OMe})_3$, no significant effect on the electrochemistry of **215** has been observed, but precipitation with hexane gives **217**, of which the structure has been determined.¹⁷⁸ The sodium salt of **216** produced by sodium

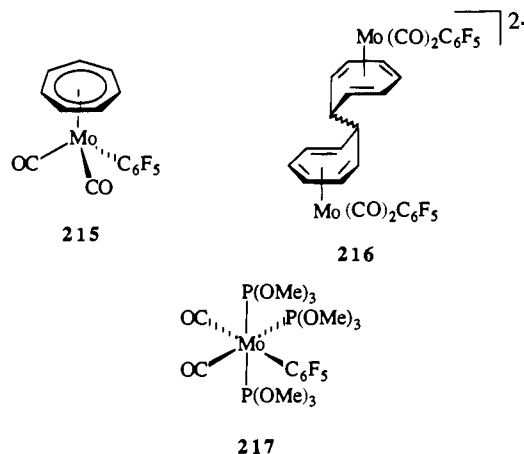
Table 2. Electrochemical Data of Half-Sandwich Cycloheptatrienyl Molybdenum and Tungsten Compounds^{135,158b}

compound	$E_{1/2}(0/+1)$ (V) ^a
$\text{Mo}(\eta^7\text{-C}_7\text{H}_7)[\text{P}(\text{OMe})_3]_2\text{I}$	0.10
$\text{Mo}(\eta^7\text{-C}_7\text{H}_7)[\text{P}(\text{OMe})_3]_2\text{Cl}$	0.00
$\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{PPh}_3)(\text{CO})\text{I}$	0.58
$\text{W}(\eta^7\text{-C}_7\text{H}_7)(\text{PPh}_3)(\text{CO})\text{I}$	0.49
$[\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{dppe})(\text{MeCN})]^+$	0.37 ^b
$[\text{W}(\eta^7\text{-C}_7\text{H}_7)(\text{dppe})(\text{MeCN})]^+$	0.23 ^b
$\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{dppe})\text{Cl}$	-0.05
$\text{W}(\eta^7\text{-C}_7\text{H}_7)(\text{dppe})\text{Cl}$	-0.21
$\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{dppe})(\text{C}\equiv\text{CPh})$	-0.15
$\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{dppe})(\text{C}\equiv\text{CBu}^t)$	-0.28

^a $E_{1/2}$ vs SCE measured in CH_2Cl_2 unless stated otherwise.

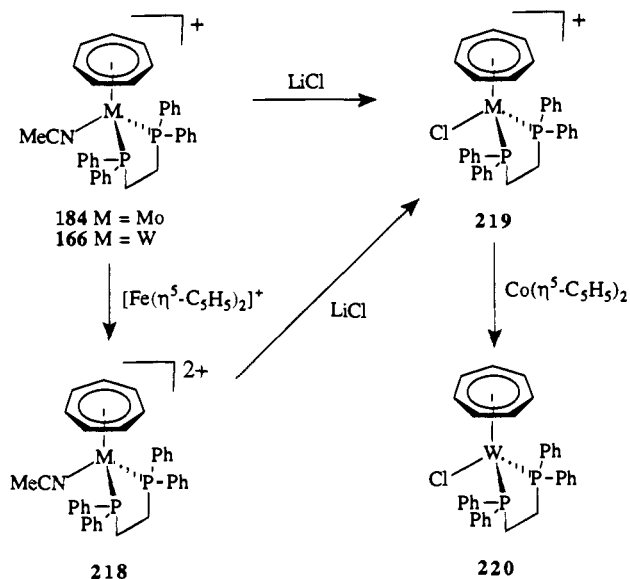
^b In MeCN.

amalgam reduction is extremely air sensitive and cannot be isolated. However, addition of $[\text{N}(\text{PPh}_3)_2]^+$ leads to an isolable salt which exists in solution as a mixture of *endo-endo*-, *endo-exo*-, and *exo-exo*-isomers, in which the *endo-endo*-isomer has been crystallographically characterized. Reoxidation of **216** rapidly cleaves the bridging C-C bond and regenerates **215**.¹⁷⁷

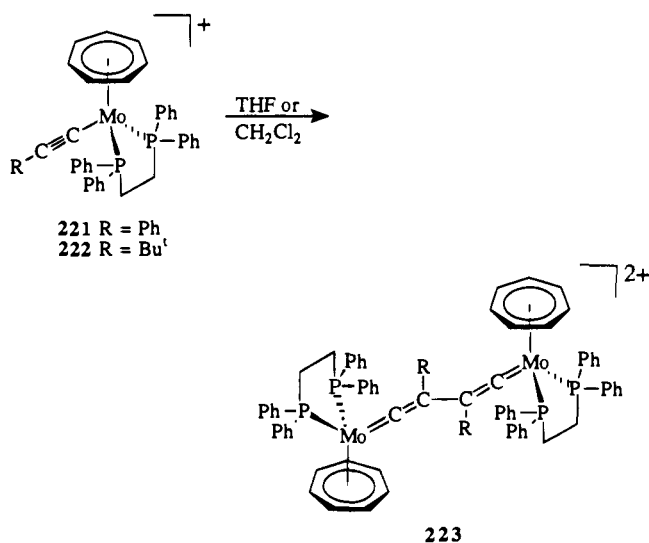


Whiteley *et al.* have investigated the electrochemistry of some half-sandwich cycloheptatrienyl derivatives of molybdenum and tungsten.^{135,158b} Table 2 lists the $E_{1/2}$ values determined by cyclic voltammetry. All of these complexes undergo a 1-electron transfer process and some of these redox processes can be performed chemically. For example, compound $\text{Mo}(\eta^7\text{-C}_7\text{H}_7)[\text{P}(\text{OMe})_3]_2\text{I}$ (**191**) can be oxidized with $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]^+$ or $[\text{NO}]^+$ to give the corresponding cation, while reduction of $\{\text{Mo}(\eta^7\text{-C}_7\text{H}_7)[\text{P}(\text{OMe})_3]_2\text{Cl}\}^+$ (**192**) with $\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2$ affords the corresponding neutral compound.¹³⁵ Ferrocenium cation can also be used as oxidant to convert $[\text{M}(\eta^7\text{-C}_7\text{H}_7)(\text{dppe})(\text{MeCN})]^+$ [$\text{M} = \text{Mo}$ (**184**) or W (**166**)] to the corresponding dication (**218**). Both of the cations **184** and **166** react with LiCl in acetone forming the paramagnetic species $[\text{M}(\eta^7\text{-C}_7\text{H}_7)(\text{dppe})\text{Cl}]^+$ (**219**). For the reaction with **166**, it requires prolonged reflux in acetone and gives $\text{W}(\eta^7\text{-C}_7\text{H}_7)(\text{dppe})\text{Cl}$ (**220**) as side product. Treatment of the dication **218** with LiCl also gives **219**, but their formation is much faster than that from the corresponding cations. Chemical reduction of **219** ($\text{M} = \text{W}$) to **220** with $\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2$ has also been reported (Scheme 89).¹³⁵

Scheme 89



Scheme 90

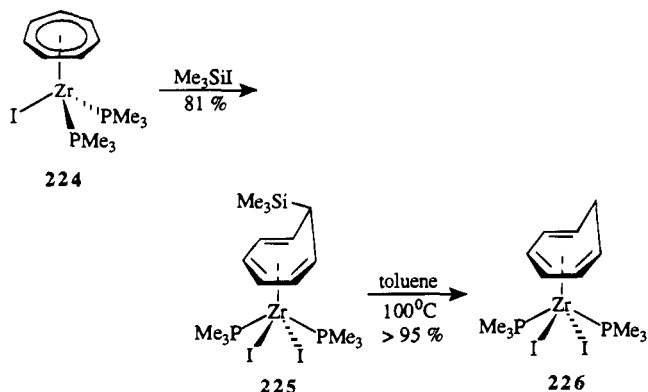


Both **187** and **188** can be oxidized with $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]^+$ to produce the corresponding cations $[\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{dppe})(\text{C}\equiv\text{CR})]^+$ [$\text{R} = \text{Ph}$ (**221**) or Bu^t (**222**)].^{158b} X-ray diffraction studies have been performed on **187** and its monocation **221** which show that the mean Mo–P distance increases and the Mo–C(alkynyl) distance decreases significantly resulting from oxidation. The mean Mo–C(ring) distance and C≡C bond length are virtually unchanged. These observations suggest that the alkynyl ligand in these complexes acts predominantly as a σ -donor to molybdenum with insignificant contribution of $d\pi$ (metal) $\rightarrow \pi^*$ (alkynyl) interaction to the metal–alkynyl bond.¹⁷⁹ Interestingly, cations **221** and **222** undergo coupling at C_β of the alkynyl ligand to form the divinylidene-bridged, dimer products **223** of which the structure for $\text{R} = \text{Ph}$ has been confirmed by X-ray studies (Scheme 90).¹⁸⁰

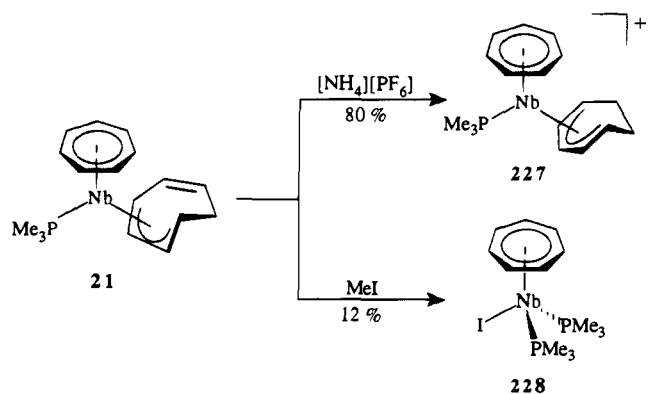
6. Other Reactions

The catalytic properties of cycloheptatrienylmetal complexes have been briefly examined. The dimer $[\text{Ti}(\eta^7\text{-C}_7\text{H}_7)(\text{THF})(\mu\text{-Cl})_2]$ (**11**) in conjunction with

Scheme 91



Scheme 92

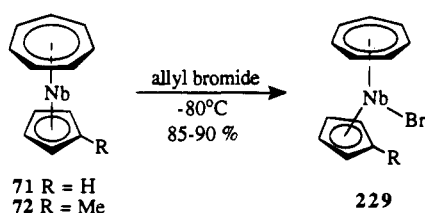


$(\text{AlEt}_2\text{Cl})_2$ catalyzes ethylene polymerization. The activity of the catalyst system is highly variable as a function of varying proportions. The best activity number for the catalyst achieved is 0.11 g of polyethylene per hour per atmosphere of ethylene per millimole of catalyst.^{22b} Recently, it has been found that the 17-electron complex $\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{MeCN})\text{I}_2$ (**197**), activated with $\text{Me}_3\text{SiCH}_2\text{MgCl}$, is a catalyst for ring-opening metathesis polymerization of norbornene. In a preliminary study, **197**/ $\text{Me}_3\text{SiCH}_2\text{MgCl}$ reacts with 300 equiv of norbornene (2 g) in toluene at room temperature for 17 h produces 0.2 g of polynorbornene. Noteworthy, essentially all of the double bonds in the polymer are in the *trans*-configuration as determined by ¹³C NMR spectroscopy. The tungsten analog $\text{W}(\eta^7\text{-C}_7\text{H}_7)(\text{MeCN})\text{I}_2$ (**209**) behaves in a similar manner, except that the reactivity of this catalyst system is higher (1 g of norbornene gives 0.58 g of polymer under similar conditions) and the selectivity is lower (the resulting polymer has a *trans*:*cis* ratio of 2.2:1).¹⁶⁴

The reaction of $\text{Zr}(\eta^7\text{-C}_7\text{H}_7)(\text{PMe}_3)_2\text{I}$ (**224**) with Me_3SiI unexpectedly produces the crystallographically characterized *exo*-substituted cycloheptatriene complex **225** in high yield. This compound is thermally sensitive, and upon heating in toluene at 100 °C gives **226** (Scheme 91). When perdeuteriotoluene is used as solvent there is no observable incorporation of deuterium into **226**.^{26b,27}

Protonation of **21** with $[\text{NH}_4][\text{PF}_6]$ affords good yields of **227**, whereas reaction of **21** with iodomethane gives the unexpected paramagnetic compound **228** in 12% yield (Scheme 92). The X-ray structure of **228** has been determined. The sandwich compounds **71** and **72** react with 1 equiv of allyl

Scheme 93



bromide at $-80\text{ }^{\circ}\text{C}$ yielding the bent mixed-sandwich compounds **229** in excellent yield (Scheme 93).³⁵

VII. Concluding Remarks

A rich and diverse chemistry of the cycloheptatriene and -enyl compounds of the early transition metals has been developed in the period covered in this article. The preparations of many useful syntheses have been discovered and the nature of the η -cycloheptatrienyl-transition metal bonding has been clarified. There are clearly many possibilities for the future development of the chemistry of η -cycloheptatrienyl complexes. Applications in homogeneous catalysis have been little studied but it seems probable that the unique properties of the η -cycloheptatrienyl ligand will find a role in this area. Also, there remains the challenge to develop areas such as η -cycloheptatrienyl-lanthanide chemistry, for example, neutral compounds in the general class $[\text{M}(\eta\text{-C}_7\text{H}_7)\text{L}_3]$, where L is a 2-electron donor ligand. η -Cycloheptatrienyl transition metal systems in combination with other hydrocarbyl ligands such as carbenes, carbynes, polyhydrides are either unknown or scarcely studied. We hope this article will stimulate further research into C₇-ring chemistry.

VIII. Acknowledgements

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IX. References

- Moser, W. R.; Slocum, D. W., Eds. *Homogeneous Transition Metal Catalyzed Reactions*; American Chemical Society: Washington, DC, 1992.
- Hegedus, L. S. *Transition Metals in the Synthesis of Complex Organic Molecules*; University Science: California, 1994.
- Bruce, D. W.; O'Hare, D., Eds. *Inorganic Materials*; Wiley: Chichester, 1992.
- (a) Yamamoto, A. *Organotransition Metal Chemistry*; Wiley: New York, 1986; pp 412-419. (b) Pöpf-Maier, P.; Köpf, H. *Struct. Bond.* **1988**, *70*, 105.
- Abel, E. W.; Bennett, M. A.; Burton, R.; Wilkinson, G. *J. Chem. Soc.* **1958**, 4559.
- Dauben, H. J.; Honnen, L. R. *J. Am. Chem. Soc.* **1958**, *80*, 5570.
- Deganello, G. *Transition Metal Complexes of Cyclic polyolefins*; Academic Press: London, 1979; Chapter 1.
- Cotton, F. A.; McCleverty, J. A.; White, J. E. *Inorg. Synth.* **1990**, *28*, 45.
- King, R. B.; Fronzaglia, A. *Inorg. Chem.* **1966**, *5*, 1837.
- Kubas, G. J. *Inorg. Chem.* **1983**, *22*, 692.
- Munro, J. D.; Pauson, P. L. *J. Chem. Soc.* **1961**, 3475.
- Green, M. L. H.; Ng, D. K. P. *J. Chem. Soc., Dalton Trans.* **1993**, 17.
- (a) Werner, R. P. M.; Manastyrskyj, S. A. *J. Am. Chem. Soc.* **1961**, *83*, 2023. (b) Calderazzo, F.; Calvi, P. L. *Chim. Ind. (Milan)* **1962**, *44*, 1217.
- Müller, J.; Mertschenk, B. *J. Organomet. Chem.* **1972**, *34*, 165.
- Blackborow, J. R.; Young, D. *Metal Vapour Synthesis in Organometallic Chemistry*; Springer-Verlag: Berlin, 1979.
- Timms, P. L.; Turney, T. W. *J. Chem. Soc., Dalton Trans.* **1976**, 2021.
- Cloke, F. G. N.; Green, M. L. H.; Lennon, P. J. *J. Organomet. Chem.* **1980**, *188*, C25.
- Tovey, R. C. D. Phil. Thesis, University of Oxford, 1986.
- Van Dam, E. M.; Brent, W. N.; Silvon, M. P.; Skell, P. S. *J. Am. Chem. Soc.* **1975**, *97*, 465.
- Blackborow, J. R.; Eady, C. R.; Koerner von Gustorf, E. A.; Scrivanti, A.; Wolfbeis, O. *J. Organomet. Chem.* **1976**, *108*, C32.
- (a) Green, M. L. H.; Newman, P. A. *J. Chem. Soc., Chem. Commun.* **1984**, 816. (b) Green, M. L. H.; Newman, P. A.; Bandy, J. A. *J. Chem. Soc., Dalton Trans.* **1989**, 331.
- (a) Green, M. L. H.; Hazel, N. J.; Grebenik, P. D.; Mtetwa, V. S. B.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1983**, 356. (b) Davies, C. E.; Gardiner, I. M.; Green, J. C.; Green, M. L. H.; Hazel, N. J.; Grebenik, P. D.; Mtetwa, V. S. B.; Prout, K. *J. Chem. Soc., Dalton Trans.* **1985**, 669.
- (a) Green, M. L. H.; O'Hare, D.; Watkin, J. G. *J. Chem. Soc., Chem. Commun.* **1989**, 698. (b) Green, M. L. H.; O'Hare, D.; Mountford, P.; Watkin, J. G. *J. Chem. Soc., Dalton Trans.* **1991**, 1705.
- (a) Green, M. L. H.; Walker, N. M. *J. Chem. Soc., Chem. Commun.* **1989**, 850. (b) Green, J. C.; Green, M. L. H.; Walker, N. M. *J. Chem. Soc., Dalton Trans.* **1991**, 173.
- Van Oven, H. O.; de Liefde Meijer, H. J. *J. Organomet. Chem.* **1971**, *31*, 71.
- (a) Diamond, G. M.; Green, M. L. H.; Walker, N. M. *J. Organomet. Chem.* **1991**, *413*, C1. (b) Diamond, G. M.; Green, M. L. H.; Mountford, P.; Walker, N. M. *J. Chem. Soc., Dalton Trans.* **1992**, 2259.
- Green, M. L. H.; Mountford, P.; Walker, N. M. *J. Chem. Soc., Chem. Commun.* **1989**, 908.
- (a) Green, M. L. H.; Walker, N. M. *J. Chem. Soc., Chem. Commun.* **1989**, 1865. (b) Diamond, G. M.; Green, M. L. H.; Mountford, P.; Walker, N. M.; Howard, J. A. K. *J. Chem. Soc., Dalton Trans.* **1992**, 417.
- Van Oven, H. O.; de Liefde Meijer, H. J. *J. Organomet. Chem.* **1970**, *23*, 159.
- Demerseman, B.; Bouquet, G.; Bigorgne, M. *J. Organomet. Chem.* **1975**, *101*, C24.
- Van Oven, H. O.; Groenenboom, C. J.; de Liefde Meijer, H. J. *J. Organomet. Chem.* **1974**, *81*, 379.
- Blenkers, J.; Bruin, P.; Teuben, J. H. *J. Organomet. Chem.* **1985**, *297*, 61.
- Kool, L. B.; Rausch, M. D.; Rogers, R. D. *J. Organomet. Chem.* **1985**, *297*, 289.
- King, R. B.; Eisch, J. *J. Organomet. Synth.* **1986**, *3*, 27.
- (a) Green, M. L. H.; Mountford, P.; Scott, P.; Mtetwa, V. S. B. *Polyhedron* **1991**, *10*, 389. (b) Green, M. L. H.; Hughes, A. K.; McGowan, P. C.; Mountford, P.; Scott, P.; Simpson, S. J. *J. Chem. Soc., Dalton Trans.* **1992**, 1591.
- Müller, J.; Goll, W. *J. Organomet. Chem.* **1974**, *71*, 257.
- Green, J. C.; Green, M. L. H.; Kaltsoyannis, N.; Mountford, P.; Scott, P.; Simpson, S. J. *Organometallics*, **1992**, *11*, 3353.
- Andras, M. T.; Duraj, S. A. *Inorg. Chem.* **1993**, *32*, 2874.
- (a) Fischer, E. O.; Müller, J. *Z. Naturforsch.* **1963**, *18B*, 1137. (b) Wehner, H. W.; Fischer, E. O.; Müller, J. *Chem. Ber.* **1970**, *103*, 2258.
- Green, M. L. H.; Ng, D. K. P.; Scott, P. Unpublished results.
- (a) Green, M. L. H.; Ng, D. K. P.; Tovey, R. C. *J. Chem. Soc., Chem. Commun.* **1992**, 918. (b) Green, M. L. H.; Ng, D. K. P.; Tovey, R. C.; Chernega, A. N. *J. Chem. Soc., Dalton Trans.* **1993**, 3203.
- (a) Green, M. L. H.; Ng, D. K. P. *J. Chem. Soc., Chem. Commun.* **1992**, 1116. (b) Green, M. L. H.; Ng, D. K. P.; Wong, H.-V. *J. Chem. Soc., Dalton Trans.* **1993**, 3213.
- Schwed, E.; Hund, H. U.; Bosch, H. W.; Berke, H. *Helv. Chim. Acta* **1991**, *74*, 189.
- Green, M. L. H.; Siriwardene, D. K.; O'Hare, D.; Wong, L.-L. *J. Chem. Soc., Dalton Trans.* **1988**, 2851.
- Dunitz, J. D.; Pauling, P. *Helv. Chim. Acta* **1960**, *43*, 2188.
- Hadley, F. J.; Gilbert, T. M.; Rogers, R. D. *J. Organomet. Chem.* **1993**, *455*, 107.
- Reynolds, S. D.; Albright, T. A. *Organometallics* **1985**, *4*, 980.
- (a) Mawhorter, R. J.; Rankin, D. W. H.; Robertson, H. E.; Green, M. L. H.; Scott, P. *Organometallics* **1994**, *13*, 2401. (b) Green, M. L. H.; Mountford, P.; Mtetwa, V. S. B.; Scott, P.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* **1992**, 314.
- Elian, M.; Chen, M. M. L.; Mingos, D. M. P.; Hoffmann, R. *Inorg. Chem.* **1976**, *15*, 1148.
- Rogers, R. D.; Teuben, J. H. *J. Organomet. Chem.* **1988**, *354*, 169.
- Harvey, P. D.; Butler, I. S.; Gilson, D. F. R. *Inorg. Chem.* **1987**, *26*, 32.
- Mingos, D. M. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol 3, pp 1-88.
- Jarrett-Sprague, S. A.; Hillier, I. H. *Int. J. Mass Spectrom. Ion Processes* **1992**, *122*, 349.
- Davies, S. G.; Green, M. L. H.; Mingos, D. M. P. *Tetrahedron* **1978**, *34*, 3047.

- (55) Groenenboom, C. J.; Sawatzky, G.; de Liefde Meijer, H. J.; Jellinek, F. *J. Organomet. Chem.* **1974**, *76*, C4.
- (56) (a) Clack, D. W.; Warren, K. D. *Theor. Chim. Acta* **1977**, *46*, 313. (b) Zeinstra, J. D.; Nieuwpoort, W. C. *Inorg. Chim. Acta* **1978**, *30*, 103.
- (57) Groenenboom, C. J.; de Liefde Meijer, H. J.; Jellinek, F. *J. Organomet. Chem.* **1974**, *69*, 235.
- (58) Groenenboom, C. J.; Jellinek, F. *J. Organomet. Chem.* **1974**, *80*, 229.
- (59) Evans, S.; Green, J. C.; Jackson, S. E.; Higginson, B. *J. Chem. Soc., Dalton Trans.* **1974**, 304.
- (60) Green, J. C.; Kaltsoyannis, N.; Sze, K. H.; MacDonald, M. *J. Am. Chem. Soc.* **1994**, *116*, 1994.
- (61) Clack, D. W.; Warren, K. D. *Inorg. Chim. Acta* **1978**, *30*, 251.
- (62) Roth, W. R.; Grimme, W. *Tetrahedron Lett.* **1966**, 2347.
- (63) (a) Foreman, M. I.; Knox, G. R.; Pauson, P. L.; Todd, K. H.; Watts, W. E. *J. Chem. Soc., Chem. Commun.* **1970**, 843. (b) Foreman, M. I.; Knox, G. R.; Pauson, P. L.; Todd, K. H.; Watts, W. E. *J. Chem. Soc., Dalton Trans.* **1972**, 1141.
- (64) Brown, J. M.; Midgley, I.; Albery, W. J. *J. Chem. Soc., Perkin Trans. 2* **1982**, 767.
- (65) Hooker, R. H.; Rest, A. J. *J. Organomet. Chem.* **1982**, *234*, C23.
- (66) Houk, K. N.; Woodward, R. B. *J. Am. Chem. Soc.* **1970**, *92*, 4143.
- (67) For a review, see: Kreiter, C. G. *Adv. Organomet. Chem.* **1986**, *26*, 297.
- (68) (a) Ozkar, S.; Kurz, H.; Neugebauer, D.; Kreiter, C. G. *J. Organomet. Chem.* **1978**, *160*, 115. (b) Kreiter, C. G.; Kurz, H. *Chem. Ber.* **1983**, *116*, 1494. (c) Ozkar, S.; Kreiter, C. G. *J. Organomet. Chem.* **1985**, *293*, 229.
- (69) Rigby, J. H. *Acc. Chem. Res.* **1993**, *26*, 579.
- (70) Rigby, J. H.; Ateeq, H. S.; Charles, N. R.; Cuisiat, S. V.; Ferguson, M. D.; Henshilwood, J. A.; Krueger, A. C.; Ogbu, C. O.; Short, K. M.; Heeg, M. J. *J. Am. Chem. Soc.* **1993**, *115*, 1382.
- (71) Rigby, J. H.; Ateeq, H. S. *J. Am. Chem. Soc.* **1990**, *112*, 6442.
- (72) (a) Michels, E.; Kreiter, C. G. *J. Organomet. Chem.* **1983**, *252*, C1. (b) Michels, E.; Sheldrick, W. S.; Kreiter, C. G. *Chem. Ber.* **1985**, *118*, 964.
- (73) Van Houwelingen, T.; Stufkens, D. J.; Oskam, A. *Organometallics* **1992**, *11*, 1146.
- (74) Brown, D. L. S.; Connor, J. A.; Demain, C. P.; Leung, M. L.; Martinho-Simoes, J. A.; Skinner, H. A.; Zafarani Moattar, M. T. *J. Organomet. Chem.* **1977**, *142*, 321.
- (75) Rigby, J. H.; Henshilwood, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 5122.
- (76) Rigby, J. H.; Ateeq, H. S.; Charles, N. R.; Henshilwood, J. A.; Short, K. M.; Sugathapala, P. M. *Tetrahedron* **1993**, *49*, 5495.
- (77) Rigby, J. H.; Short, K. M.; Ateeq, H. S.; Henshilwood, J. A. *J. Org. Chem.* **1992**, *57*, 5290.
- (78) (a) Mach, K.; Antropiusová, H.; Sedmera, P.; Hanuš, V.; Tureček, F. *J. Chem. Soc., Chem. Commun.* **1983**, 805. (b) Klein, R.; Sedmera, P.; Čejka, J.; Mach, K. *J. Organomet. Chem.* **1992**, *436*, 143.
- (79) Fischler, I.; Grevels, F.-W.; Leitich, J.; Özkar, S. *Chem. Ber.* **1991**, *124*, 2857.
- (80) Chaffee, K.; Sheridan, J. B.; Aistars, A. *Organometallics* **1992**, *11*, 18.
- (81) (a) Mukerjee, S. L.; Lang, R. F.; Ju, T.; Kiss, G.; Hoff, C. D.; Nolan, S. P. *Inorg. Chem.* **1992**, *31*, 4885. (b) Nolan, S. P.; de la Vega, R. L.; Hoff, C. D. *Organometallics* **1986**, *5*, 2529. (c) Hoff, C. D. *J. Organomet. Chem.* **1983**, *246*, C53.
- (82) (a) Strohmeier, W.; von Hobe, D. Z. *Naturforsch.* **1963**, *18b*, 981. (b) Pidcock, A.; Taylor, B. W. *J. Chem. Soc. (A)* **1967**, 877. (c) Al-Kathumi, K. M.; Kane-Maguire, L. A. P. *J. Chem. Soc., Dalton Trans.* **1974**, 428.
- (83) Wasserman, H. J.; Kubas, G. J.; Ryan, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2294.
- (84) Kubas, G. J.; Unkefer, C. J.; Swanson, B. I.; Fukushima, E. *J. Am. Chem. Soc.* **1986**, *108*, 7000.
- (85) Gonzalez, A. A.; Mukerjee, S. L.; Chou, S.-J.; Kai, Z.; Hoff, C. D. *J. Am. Chem. Soc.* **1988**, *110*, 4419.
- (86) (a) Dunbar, K. R.; Sun, J.-S.; Haefner, S. C.; Matonic, J. H. *Organometallics* **1994**, *13*, 2713. (b) Bagchi, R. N.; Bond, A. M.; Colton, R.; Creece, I.; McGregor, K.; Whyte, T. *Organometallics* **1991**, *10*, 2611.
- (87) Mague, J. T.; Johnson, M. P. *Organometallics* **1990**, *9*, 1254.
- (88) Mague, J. T.; Johnson, M. P. *Organometallics* **1991**, *10*, 349.
- (89) (a) Gamper, S. F.; Schmidbaur, H. *Organometallics* **1992**, *11*, 2863. (b) Charles, S.; Eichhorn, B. W.; Rheingold, A. L.; Bott, S. G. *J. Am. Chem. Soc.* **1994**, *116*, 8077.
- (90) (a) Hahn, F. E.; Tamm, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 203. (b) Hahn, F. E.; Tamm, M. *Organometallics* **1992**, *11*, 84. (c) Hahn, F. E. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 650. (d) Hahn, F. E.; Tamm, M. *J. Organomet. Chem.* **1994**, *467*, 103. (e) Hahn, F. E.; Tamm, M. *Organometallics* **1994**, *13*, 3002.
- (91) Sánchez-Peláez, A. E.; Perpiñán, M. F. *J. Organomet. Chem.* **1991**, *405*, 101.
- (92) King, R. B.; Pannell, K. H. *Inorg. Chem.* **1968**, *7*, 273.
- (93) (a) Anderson, W. P.; Blenderman, W. G.; Drews, K. A. *J. Organomet. Chem.* **1972**, *42*, 139. (b) Djazayeri, M.; Kreiter, C. G.; Kurz, H. M.; Lang, M.; Ozkar, S. Z. *Naturforsch* **1976**, *31b*, 1238.
- (94) Bloyce, P. E.; Hooker, R. H.; Rest, A. J.; Bitterwolf, T. E.; Fitzpatrick, N. J.; Shade, J. E. *J. Chem. Soc., Dalton Trans.* **1990**, 833.
- (95) Hooker, R. H.; Rest, A. J. *J. Chem. Soc., Dalton Trans.* **1982**, 2029.
- (96) Özer, Z.; Özkar, S.; Onal, A. M. *Inorg. Chim. Acta* **1989**, *156*, 281.
- (97) (a) Salzer, A.; Werner, H. *J. Organomet. Chem.* **1975**, *87*, 101. (b) Salzer, A.; Werner, H. Z. *Anorg. Allg. Chem.* **1975**, *418*, 88.
- (98) (a) Hinchliffe, J. R.; Whiteley, M. W. *J. Organomet. Chem.* **1991**, *402*, C50. (b) Beddoes, R. L.; Hinchliffe, J. R.; Whiteley, M. W. *J. Chem. Soc., Dalton Trans.* **1993**, 501. (c) Wang, C.; Sheridan, J. B. *Organometallics* **1994**, *13*, 3639.
- (99) Wadeplol, H.; Galm, W.; Pritzkow, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 345.
- (100) (a) Bennett, M. J.; Pratt, J. L.; Simpson, K. A.; LiShingMan, L. K. K.; Takats, J. *J. Am. Chem. Soc.* **1976**, *98*, 4810. (b) Salzer, A.; Egolf, T.; von Philipsborn, W. *Helv. Chim. Acta* **1982**, *65*, 1145. (c) Moll, M.; Behrens, H.; Popp, W.; Liehr, G.; Fehlhammer, W. P. Z. *Naturforsch.* **1983**, *38b*, 1446. (d) Ball, R. G.; Edelmann, F.; Kiel, G.-Y.; Takats, J.; Drews, R. *Organometallics* **1986**, *5*, 829. (e) Edelmann, F.; Takats, J. *J. Organomet. Chem.* **1988**, *344*, 351. (f) Edelmann, F.; Kiel, G.-Y.; Takats, J.; Vasudevamurthy, A.; Yeung, M.-Y. *J. Chem. Soc., Chem. Commun.* **1988**, 296.
- (101) (a) Jiabi, C.; Jienguo, Y.; Guixin, L.; Weihua, X.; Meicheng, S.; Zeying, Z.; Youqi, T. *J. Organomet. Chem.* **1987**, *329*, 69. (b) Kan, Z.; Taylor, S. M.; Comisarow, M. B. *J. Am. Chem. Soc.* **1994**, *116*, 4449.
- (102) (a) Demerseman, B.; Dixneuf, P. H. *J. Organomet. Chem.* **1981**, *210*, C20. (b) Demerseman, B.; Dixneuf, P. H.; Douglade, J.; Mercier, R. *Inorg. Chem.* **1982**, *21*, 3942.
- (103) Kool, L. B.; Ogasa, M.; Rausch, M. D.; Rogers, R. D. *Organometallics* **1989**, *8*, 1785.
- (104) Ogasa, M.; Rausch, M. D.; Rogers, R. D. *J. Organomet. Chem.* **1991**, *403*, 279.
- (105) Rausch, M. D.; Ogasa, M.; Ayers, M. A.; Rogers, R. D.; Rollins, A. N. *Organometallics* **1991**, *10*, 2481.
- (106) (a) Rausch, M. D.; Ogasa, M.; Rogers, R. D.; Rollins, A. N. *Organometallics* **1991**, *10*, 2084. (b) Fierro, R.; Rausch, M. D.; Rogers, R. D.; Herberhold, M. *J. Organomet. Chem.* **1994**, *472*, 87.
- (107) Glynn, R. E.; LaRoche, L. A.; Healey, D. P.; Kool, L. B. *Book of Abstracts*, 199th Meeting of the American Chemical Society, Boston, MA, Spring 1990; American Chemical Society: Washington, DC, 1990; INOR 214.
- (108) Breeze, R.; Plant, M. S.; Ricalton, A.; Sutton, D. J.; Whiteley, M. W. *J. Organomet. Chem.* **1988**, *356*, 343.
- (109) (a) Deganello, G.; Boschi, T.; Toniolo, L.; Albertin, G. *Inorg. Chim. Acta* **1974**, *10*, L3. (b) Isaacs, E. E.; Graham, W. A. G. *J. Organomet. Chem.* **1975**, *90*, 319.
- (110) Odiaka, T. I.; Kane-Maguire, L. A. P. *J. Organomet. Chem.* **1985**, *284*, 35.
- (111) (a) Brown, D. A.; Fitzpatrick, N. J.; Glass, W. K.; Taylor, T. H. *J. Organomet. Chem.* **1984**, *275*, C9. (b) Brown, D. A.; Fitzpatrick, N. J.; Glass, W. K.; Taylor, T. H. *Organometallics* **1986**, *5*, 158.
- (112) Brown, D. A.; Fitzpatrick, N. J.; McGinn, M. A. *J. Organomet. Chem.* **1984**, *275*, C5. (b) Brown, D. A.; Fitzpatrick, N. J.; McGinn, M. A.; Taylor, T. H. *Organometallics* **1986**, *5*, 152.
- (113) Powell, P.; Stephens, M.; Yassin, K. H. *J. Organomet. Chem.* **1986**, *301*, 313.
- (114) Bunton, C. A.; Lal, K.; Watts, W. E. *J. Organomet. Chem.* **1983**, *247*, C14.
- (115) Bunton, C. A.; Mhala, M. M.; Moffatt, J. R.; Watts, W. E. *J. Organomet. Chem.* **1983**, *253*, C33.
- (116) Brown, D. A.; Burns, J.; El-Gamati, I.; Glass, W. K.; Kreddan, K.; Salama, M.; Cunningham, D.; Higgins, T.; McArdle, P. *J. Chem. Soc., Chem. Commun.* **1992**, 701.
- (117) Yeh, M.-C. P.; Chuang, C.-N. *J. Chem. Soc., Chem. Commun.* **1994**, 703.
- (118) Müller, H.-J.; Nagel, U.; Steimann, M.; Polborn, K.; Beck, W. *Chem. Ber.* **1989**, *122*, 1387.
- (119) Niemer, B.; Breimair, J.; Volkel, T.; Wagner, B.; Polborn, K.; Beck, W. *Chem. Ber.* **1991**, *124*, 2237.
- (120) Wieser, M.; Sünkel, K.; Robl, C.; Beck, W. *Chem. Ber.* **1992**, *125*, 1369.
- (121) Wieser, M.; Karaghiosoff, K.; Beck, W. *Chem. Ber.* **1993**, *126*, 1081.
- (122) Breimair, J.; Wieser, M.; Wagner, B.; Polborn, K.; Beck, W. *J. Organomet. Chem.* **1991**, *421*, 55.
- (123) Adams, H.; Bailey, N. A.; Gauntlett, J. T.; Winter, M. J.; Woodward, S. J. *J. Chem. Soc., Dalton Trans.* **1991**, 2217.
- (124) Beall, T. W.; Houk, L. W. *Inorg. Chem.* **1973**, *12*, 1979.
- (125) Breeze, R.; Endud, S.; Whiteley, M. W. *J. Organomet. Chem.* **1986**, *302*, 371.

- (126) Brown, R. A.; Endud, S.; Friend, J.; Hill, J. M.; Whiteley, M. W. *J. Organomet. Chem.* **1988**, *339*, 283.
- (127) Breeze, R.; Ricalton, A.; Whiteley, M. W. *J. Organomet. Chem.* **1987**, *327*, C29.
- (128) Hinchliffe, J. R.; Ricalton, A.; Whiteley, M. W. *Polyhedron* **1991**, *10*, 267.
- (129) King, R. B.; Hoff, C. D. *J. Organomet. Chem.* **1982**, *225*, 245.
- (130) Duraj, S. A.; Andras, M. T.; Rihter, B. *Book of Abstracts*, 197th National Meeting of the American Chemical Society, Dallas, TX, Spring 1989; American Chemical Society: Washington, DC, 1989; INOR 169.
- (131) Hackett, P.; Jaouen, G. *Inorg. Chim. Acta* **1975**, *12*, L19.
- (132) Panter, V. R.; Ziegler, M. L. *Z. Anorg. Allg. Chem.* **1979**, *453*, 14.
- (133) (a) Salzer, A. *Inorg. Chim. Acta* **1976**, *17*, 221. (b) Sweigart, D. A.; Gower, M.; Kane-Maguire, L. A. P. *J. Organomet. Chem.* **1976**, *108*, C15.
- (134) Odiaka, T. I. *Inorg. Chim. Acta* **1985**, *103*, 9.
- (135) Bitcon, C.; Breeze, R.; Miller, P. F.; Whiteley, M. W. *J. Organomet. Chem.* **1989**, *364*, 181.
- (136) Grime, R. W.; Whiteley, M. W. *J. Chem. Soc., Dalton Trans.* **1994**, 1671.
- (137) See for example: (a) Rausch, M. D.; Ignatowicz, A. K.; Churchill, M. R.; O'Brien, T. A. *J. Am. Chem. Soc.* **1968**, *90*, 3242. (b) Churchill, M. R.; O'Brien, T. A. *J. Chem. Soc. (A)* **1969**, 1110. (c) King, R. B.; Bisnette, M. B. *Inorg. Chem.* **1964**, *3*, 785. (d) Isaacs, E. E.; Graham, W. A. G. *Can. J. Chem.* **1975**, *53*, 975. (e) Sasse, H. E.; Hoch, G.; Ziegler, M. L. *Z. Anorg. Allg. Chem.* **1974**, *406*, 263. (f) Ziegler, M. L.; Sasse, H. E.; Nuber, B. Z. *Naturforsch.* **1975**, *30B*, 22.
- (138) Dell, W. H.; Ziegler, M. L. *Z. Naturforsch.* **1982**, *37b*, 1.
- (139) Beddoes, R. L.; Davies, E. S.; Helliwell, M.; Whiteley, M. W. *J. Organomet. Chem.* **1991**, *421*, 285.
- (140) Chong, K. S.; Storr, A. *Can. J. Chem.* **1980**, *58*, 2278.
- (141) Chong, K. S.; Rettig, S. J.; Storr, A.; Trotter, J. *Can. J. Chem.* **1981**, *59*, 1665.
- (142) Mohr, D.; Wienand, H.; Ziegler, M. L. *J. Organomet. Chem.* **1977**, *134*, 281.
- (143) (a) Benson, I. B.; Knox, S. A. R.; Naish, P. J.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1978**, 878. (b) Benson, I. B.; Knox, S. A. R.; Naish, P. J.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1981**, 2235.
- (144) Rettenmeier, V. A.; Weidenhammer, K.; Ziegler, M. L. *Z. Anorg. Allg. Chem.* **1981**, *473*, 91.
- (145) Dell, W. H.; Ziegler, M. L. *Z. Naturforsch.* **1982**, *37b*, 7.
- (146) Green, M. L. H.; Leung, W. -H.; Ng, D. K. P. *J. Organomet. Chem.* **1993**, *460*, C4.
- (147) Ricalton, A.; Whiteley, M. W. *J. Organomet. Chem.* **1989**, *361*, 101.
- (148) Beddoes, R. L.; Ricalton, A.; Whiteley, M. W. *Acta Crystallogr., Sect. C* **1988**, *44*, 2025.
- (149) Dossett, S. J.; Hart, I. J.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1990**, 3481.
- (150) Brew, S. A.; Dossett, S. J.; Jeffery, J. C.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1990**, 3709.
- (151) Dossett, S. J.; Pilotti, M. U.; Stone, F. G. A. *Polyhedron* **1990**, *9*, 2953.
- (152) Dossett, S. J.; Hart, I. J.; Pilotti, M. U.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1991**, 511.
- (153) Green, M. L. H.; Knight, J. *J. Chem. Soc., Dalton Trans.* **1976**, 213.
- (154) Bochmann, M.; Cooke, M.; Green, M.; Kirsch, H. P.; Stone, F. G. A.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1976**, 381.
- (155) Green, M.; Kirsch, H. P.; Stone, F. G. A.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1755.
- (156) Ashworth, E. F.; Green, J. C.; Green, M. L. H.; Knight, J.; Pardy, R. B. A.; Wainwright, N. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1693.
- (157) Green, M. L. H.; Pardy, R. B. A. *Polyhedron* **1985**, *4*, 1035.
- (158) (a) Adams, J. S.; Cunningham, M.; Whiteley, M. W. *J. Organomet. Chem.* **1985**, *293*, C13. (b) Adams, J. S.; Bitcon, C.; Brown, J. R.; Collison, D.; Cunningham, M.; Whiteley, M. W. *J. Chem. Soc., Dalton Trans.* **1987**, 3049.
- (159) Green, M. L. H.; Ng, D. K. P. *J. Chem. Soc., Dalton Trans.* **1993**, 11.
- (160) Anderson, J. E.; Maher, E. T.; Kool, L. B. *Organometallics* **1991**, *10*, 1248.
- (161) Andréa, R. R.; Terpstra, A.; Oskam, A.; Bruin, P.; Teuben, J. H. *J. Organomet. Chem.* **1986**, *307*, 307.
- (162) Groenenboom, C. J.; de Liefde Meijer, H. J.; Jellinek, F.; Oskam, A. *J. Organomet. Chem.* **1975**, *97*, 73.
- (163) Elschenbroich, C.; Bilger, E.; Metz, B. *Organometallics* **1991**, *10*, 2823.
- (164) Ng, D. K. P. D. Phil. Thesis, University of Oxford, 1993.
- (165) Gourier, D.; Samuel, E. *Inorg. Chem.* **1988**, *27*, 3018.
- (166) Müller, J.; Göser, P.; Laubereau, P. *J. Organomet. Chem.* **1968**, *14*, P7.
- (167) Ketkov, S. Y. *J. Organomet. Chem.* **1992**, *429*, C38.
- (168) Wehner, H. W.; Fischer, E. O.; Müller, J. *Chem. Ber.* **1970**, *103*, 2258.
- (169) Gourdon, A.; Prout, K. *Acta Crystallogr., Sect. B* **1982**, *38*, 1596.
- (170) Green, M. L. H.; Harrison, A.; Mountford, P.; Ng, D. K. P. *J. Chem. Soc., Dalton Trans.* **1993**, 2215.
- (171) Romanin, A. M.; Venzo, A.; Ceccon, A. *J. Electroanal. Chem.* **1980**, *112*, 147.
- (172) Romanin, A. M.; Ceccon, A.; Venzo, A. *J. Electroanal. Chem.* **1981**, *130*, 245.
- (173) Armstead, J. A.; Cox, D. J.; Davis, R. *J. Organomet. Chem.* **1982**, *236*, 213.
- (174) Olgemöller, B.; Beck, W. *Chem. Ber.* **1981**, *114*, 867.
- (175) Adams, H.; Bailey, N. A.; Willett, D. G.; Winter, M. J. *J. Organomet. Chem.* **1987**, *333*, 61.
- (176) Gipson, S. L.; Kneten, K. *Inorg. Chim. Acta* **1989**, *157*, 143.
- (177) Su, M.; Gipson, S. L.; Mullica, D. F.; Sappenfield, E. L.; Leschnitzer, D. H. *J. Chem. Soc., Dalton Trans.* **1993**, 3323.
- (178) Gipson, S. L.; Mullica, D. F.; Sappenfield, E. L.; Hander, M. L.; Leschnitzer, D. H. *J. Chem. Soc., Dalton Trans.* **1992**, 521.
- (179) Beddoes, R. L.; Bitcon, C.; Whiteley, M. W. *J. Organomet. Chem.* **1991**, *402*, 85.
- (180) Beddoes, R. L.; Bitcon, C.; Ricalton, A.; Whiteley, M. W. *J. Organomet. Chem.* **1989**, *367*, C21.

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