In memory of T. A. Stephenson

Heteronuclear Complexes containing Group 6 Transition Metals; Chemical, Spectroscopic, and Theoretical Studies on some Binuclear Complexes and the *X*-Ray Crystal Structure Determination of $[WNi(CO)_3(PPh_3)_2(\eta^5\text{-}C_5H_5)]$†

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Reactions of anions $[M(CO)_3(\eta^5\text{-}C_5H_5)]^-$ with $[NiCl_2(PPh_3)_2]$ in tetrahydrofuran afford paramagnetic, bimetallic complexes $[MNi(CO)_3(PPh_3)_2(\eta^5\text{-}C_5H_5)]$ [M = Mo (**1**) or W (**2**)], and a less stable chromium analogue [M = Cr (**3**)], as green crystalline solids. Ready cleavage of these bimetallic complexes occurs, as on reaction with CO or $Ph_2PCH_2CH_2PPh_2$, and related reactions of $[WRh(CO)_3(PPh_3)_2(\eta^5\text{-}C_5H_5)]$ (**5**) are also presented. An *X*-ray diffraction study of crystalline (**2**) [monoclinic, space group $P2_1/c$, a = 17.873(9), b = 10.156(6), c = 21.249(7) Å, β = 105.05(3)°, Z = 4] establishes the structure $[(\eta^5\text{-}C_5H_5)(OC)W(\mu\text{-}CO)_2Ni(PPh_3)_2]$ (R = 0.062, R' = 0.087) with semibridging CO groups and a relatively short W–Ni separation [2.574(3) Å]. Spectroscopic studies on complexes (**1**)—(**3**) include analyses of e.s.r. spectra both in solution, where coupling to inequivalent ^{31}P nuclei is observed, and in the solid state. Comparative extended-Hückel molecular orbital studies on model complexes $[MM'(CO)_3(PH_3)_2(\eta^5\text{-}C_5H_5)]$ [M = Mo, M′ = Rh; M = W, M′ = Ni or Cu (two conformers)] are discussed and the bonding analysed in terms of both direct M–M′ and semibridging M(μ-CO)M′ interactions. Cyclic voltammetry of complexes (**2**), (**5**), and $[WCu(CO)_3(PPh_3)_2(\eta^5\text{-}C_5H_5)]$ is reported and simple redox processes occur for (**2**) and (**5**).

The chemistry associated with neighbouring, electronically different metals in bi- and poly-nuclear clusters is a topic of current interest.[1,2] In this context heterobinuclear complexes serve as simple models containing an isolated pair of metal atoms. Bonding between these heteroatoms normally involves some direct metal–metal interaction which will exhibit a degree of polarity and, in many cases, there are also bridging ligands present which are likely to be asymmetric.

We have recently reported the structural characterisation and some properties of heteronuclear species $[MM'(CO)_3(PPh_3)_2(cp)]$ (M = Mo or W, M′ = Rh or Cu, cp = η^5-C_5H_5).[3] In this paper we present the synthesis, characterisation, and some physical and chemical properties of the new paramagnetic nickel complexes $[MNi(CO)_3(PPh_3)_2(cp)]$ [M = Mo (1) or W (2)], including the crystal structure of (2). A preliminary communication of some of this work has appeared.[4] These studies are complemented by further investigations on the related heterobinuclear complexes containing molybdenum or tungsten.

Several diamagnetic heterobinuclear complexes containing nickel, mainly as the Ni(cp) unit, bonded to other metals (Cr, Mo, W, Mn, Fe, Co, or Zr) have been previously reported[1,5] and very recent studies on $[MoNi(CO)_4(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)]$ may be noted.[6] Also, higher nuclearity heteroclusters containing nickel are known,[1,7] including a few paramagnetic systems.[8] However, simple paramagnetic bimetallic complexes with a NiL_n centre, comparable to Ni^I in $[NiL_3X]$ type complexes,[9] have not previously been prepared. In an earlier study of reactions of carbonylmetalate anions with $[NiX_2(PPh_3)_2]$ (X = Cl, Br, or I) no metal–metal bonded products could be isolated.[10]

Results and Discussion

Syntheses and Reactions.—Reactions of the anions $[M(CO)_3(cp)]^-$ (M = Mo or W) with $[NiCl_2(PPh_3)_2]$ in tetrahydrofuran (thf) at ambient temperature afford the bimetallic complexes $[MNi(CO)_3(PPh_3)_2(cp)]$ [M = Mo (1) or W (2)], which precipitate from solution as crude products on addition of water. Subsequent recrystallisation from dichloromethane–hexane gives the pure complexes as deep green crystals which are moderately stable on short exposures to air but are very air-sensitive in solution. Complex (2) is the more stable and may be isolated in reasonable yields (>50%), whereas (1) decomposes more readily and losses during purification procedures lead to lower yields of pure product (*ca.* 20%). In these syntheses the Ni^{II} of the starting complex is reduced to a formal Ni^0 state and by-products of the reactions are $[M_2(CO)_6(cp)_2]$ (M = Mo or W) and $[Ni(CO)_2(PPh_3)_2]$. Other by-products are also obtained in smaller amounts and species which have been unambiguously identified are $[WCl(CO)_2(PPh_3)(cp)]$[11] and $[Mo_2(CO)_5(PPh_3)(cp)_2]$.[12]

A related reaction between $Na[Cr(CO)_3(cp)]$ and $[NiCl_2(PPh_3)_2]$ affords a similar green product which is very air-sensitive; spectroscopic data for this chromium species are analogous to those of complexes (1) and (2) and support the formulation $[CrNi(CO)_3(PPh_3)_2(cp)]$ (3) but analytically pure material could not be obtained: decomposition occurred during attempted purification procedures resulting in the formation of Cr^{II} products and $[Ni(CO)_2(PPh_3)_2]$.

In solution, the binuclear complexes (1) and (2) are decomposed by air with rupture of the bimetallic unit. The only identified nickel species, obtained as a major product, is $[Ni(CO)_2(PPh_3)_2]$ and this is accompanied by uncharacterised, oxidised cyclopentadienyl species of the Group 6A metals. It is of interest that previous studies on reactions of $[NiX_2(PPh_3)_2]$ with carbonylmetalate anions afforded only mononuclear $[Ni(CO)_2(PPh_3)_2]$.[10] Carbon monoxide reacts rapidly with solutions of these complexes. Thus, complex (2) in dichloromethane solution with CO (1 atm, 20 °C) also forms

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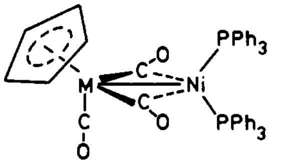
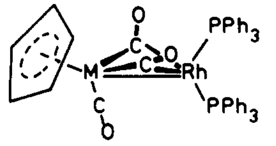
† Di-μ-carbonyl-2-carbonyl-2-(η^5-cyclopentadienyl)-1,1-bis(triphenylphosphine)nickeltungsten (*Ni–W*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Non-S.I. units employed: atm = 101 325 Pa, eV ≈ 1.60×10^{-19} J, B.M. = 0.927×10^{-23} A m^2.



M
(1) Mo
(2) W
(3) Cr



M
(4) Mo
(5) W

$[Ni(CO)_2(PPh_3)_2]$ with the tungsten dimer $[W_2(CO)_6(cp)_2]$ as co-product; other products formed in smaller amounts (identified by i.r. spectroscopy) are $[Ni(CO)_3(PPh_3)]$ and $[WCl(CO)_3(cp)]$, the latter probably resulting from radical attack on the solvent. Reaction of (2) with 1,2-bis(diphenylphosphino)ethane (dppe) also cleaves the binuclear system forming $[W_2(CO)_6(cp)_2]$ as the major, isolable tungsten species. In all of these reactions the bimetallic system appears to be fragmenting initially into Ni^0 and a reactive W^I radical which undergoes dimerisation or further reaction.

Photolysis (medium pressure Hg lamp, Pyrex filter) of complex (1) in the absence of air but in the presence of nitrosodurene (1,2,4,5-tetramethyl-3-nitrosobenzene) in dichloromethane solution at -40 °C forms a paramagnetic nitroxide with solution e.s.r. parameters identical to those assigned to $[Mo(NOC_6Me_4H\text{-}p)(CO)_n(cp)]$ ($n \leqslant 3$).[13] This species has also been observed on similar photolyses of $[MoRh(CO)_3(PPh_3)_2(cp)]$ (4).[3] Again the binuclear unit is cleaved and this result is consistent with the formation and subsequent trapping of the species $[Mo(CO)_3(cp)]$; however, in both this and the former cleavage reactions such *free* radicals may not be formed and the products may result from reagent attack on the binuclear complex.

The related rhodium complex $[WRh(CO)_3(PPh_3)_2(cp)]$ (5), which formally possesses a multiple metal–metal bond,[3] also reacts readily with CO and with dppe. Excess dppe in solution at ambient temperature produces $[Rh(dppe)_2][W(CO)_3(cp)]$ (6), isolable as a yellow solid solvated with CH_2Cl_2. Complex (6), at least in solution, appears to be a simple ionic product since i.r. and ^1H and ^{31}P n.m.r. spectra are assignable to the free ions $[Rh(dppe)_2]^+$ [14] and $[W(CO)_3(cp)]^-$,[15] interacting as an ion pair. In this reaction the binuclear complex is cleaved heterolytically. Admission of CO to (5) in various solvents causes facile reactions: the dark brown solutions turn light red-orange giving a new product with distinctive ν(CO) bands (see Experimental section). Evaporation of these solutions to dryness causes reformation of (5) and solids obtained by precipitation or crystallisation after addition of hexane are complex (5) and/or solvated rhodium carbonyl–phosphine species $[Rh(CO)_n(PPh_3)_2(sol)_m]$, first described by Wilkinson and co-workers.[16] The most probable explanation for these observations is that reversible addition of CO to (5) forms $[(cp)(OC)_3WRh(CO)(PPh_3)_2]$ which is prone to decomposition by W–Rh bond cleavage. This adduct is related to species

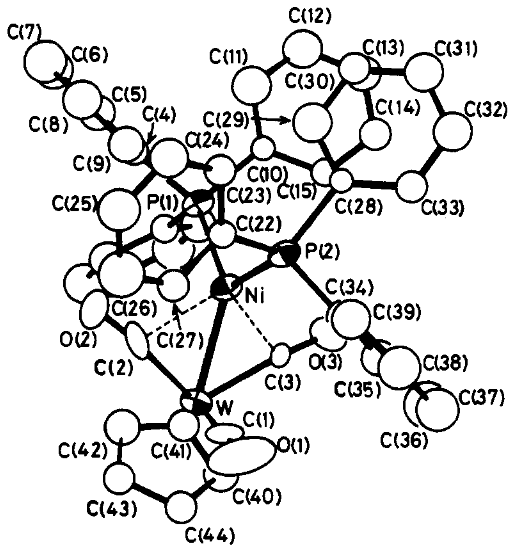


Figure 1. Molecular structure of complex (2) (ORTEP)

$[(OC)_3Mo(\mu\text{-}\eta^5\text{-}\overline{C_5H_4PPh_2)Rh}(CO)(PR_3)]$ (R = Me or C_6H_4Me-*p*) previously reported by Casey *et al.*[17] It is of interest that ready cleavage or disproportionation of the metal systems of complexes (4) and (5) on reaction with $[Fe_2(CO)_9]$ or $[Pt(C_2H_2)(PPh_3)_2]$ has been reported.[18]

Molecular Structure of $[WNi(CO)_3(PPh_3)_2(cp)]$ (2).—A small dark green prismatic crystal of (2), obtained from CH_2Cl_2–hexane at -20 °C was subjected to *X*-ray crystallographic analysis. Figure 1 presents a perspective view of a single molecule of complex (2). Tables 1 and 2, respectively, list atomic fractional co-ordinates and important derived geometrical parameters. In the solid state, complex (2) possesses no inherent point symmetry; the planes defined by atoms W, Ni, C(1), O(1) and Ni, P(1), P(2) make an angle of 10.9°.

The bonding of the cyclopentadienyl group to W is normal for η^5 co-ordination, although the ligand does show rotational disorder with 55:45% occupancy of two sites. Figure 1 depicts the site of major occupancy. The Ni–P distances are intermediate between those of $[NiBr(PPh_3)_3]$ [9c] and $[Ni(CO)_2(PPh_3)_2]$ [19] and the angle P(1)–Ni–P(2) is closer to tetrahedral than trigonal. The two P atoms are inequivalent which is consistent with the e.s.r. spectrum (see below) so that any fluxionality must be frozen out on the e.s.r. time-scale.

The three CO ligands approach linear co-ordination to W (W–C–O $\geqslant$ 167°). The C(1)O(1) ligand is a normal terminal ligand with the shortest W–C bond [1.945(23) Å] and largest W–C–O angle [175.4(20)°]. Both C(2)–O(2) and C(3)–O(3) are similarly located and approach close to Ni [Ni–C 2.122(21) and 2.086(19) Å]. These Ni–C distances are longer than in $[Ni_2(\mu\text{-}CO)_2(cp)_2]$,[5a,20] significantly shorter than in $[NiCr(\mu\text{-}CO)_2(CO)(cp)_2]$,[5a] and comparable to those in $[Ni\{W(\mu\text{-}CC_6H_4Me\text{-}p)(\mu\text{-}CO)(CO)(cp)\}_2]$ [21] so that semibridging interactions between both C(2)–O(2) and C(3)–O(3) and the Ni atom must occur. The nature of semibridging CO interactions has recently been discussed by Crabtree and Lavin[22] and in the context of that paper the structural parameters of these CO groups approximate to normal 'bent' (166°) semibridging groups. The Ni atom is virtually in the plane W,C(2),C(3) [interplanar angle W–C(2)–Ni/W–C(3)–Ni 168.3°] being structurally analogous to the red-orange isomer of $[WCu(CO)_3(PPh_3)_2(cp)]$ (7), reported earlier.[3] However, the Ni–W and Ni–C(2,3) bonds in (2) are significantly shorter than the corresponding Cu–W and Cu–C(2,3) distances in (7). The Ni–W

Table 1. Fractional atomic co-ordinates, with estimated standard deviations in parentheses, for complex (**2**)*

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W(1)	0.889 79(5)	0.639 28(9)	0.405 68(4)	C(13)	0.532 0(8)	0.510 6(12)	0.094 3(7)
Ni(1)	0.777 91(14)	0.489 73(24)	0.345 14(11)	C(14)	0.559 5(8)	0.588 8(12)	0.149 5(7)
P(1)	0.767 8(3)	0.423 2(5)	0.241 02(24)	C(15)	0.630 4(8)	0.559 8(12)	0.193 2(7)
P(2)	0.680 9(3)	0.401 3(5)	0.383 60(24)	C(10)	0.673 9(8)	0.452 5(12)	0.181 8(7)
C(1)	0.858 8(12)	0.597 4(21)	0.484 6(11)	C(17)	0.816 4(7)	0.607 2(15)	0.160 3(7)
O(1)	0.840 8(14)	0.581 1(20)	0.533 3(7)	C(18)	0.873 2(7)	0.676 0(15)	0.139 6(7)
C(2)	0.896 2(10)	0.450 1(24)	0.390 4(9)	C(19)	0.951 3(7)	0.644 8(15)	0.165 2(7)
O(2)	0.911 1(9)	0.341 1(15)	0.382 6(7)	C(20)	0.972 4(7)	0.544 9(15)	0.211 4(7)
C(3)	0.784 3(11)	0.693 7(18)	0.356 8(9)	C(21)	0.915 6(7)	0.476 1(15)	0.232 1(7)
O(3)	0.730 1(9)	0.744 4(16)	0.325 2(8)	C(16)	0.837 5(7)	0.507 3(15)	0.206 6(7)
C(40)	0.936 1(16)	0.849(3)	0.407 5(25)	C(23)	0.664 6(6)	0.124 7(13)	0.399 4(5)
C(41)	0.948 8(16)	0.782(3)	0.352 6(25)	C(24)	0.691 2(6)	0.003 4(13)	0.427 2(5)
C(42)	1.002 7(16)	0.679(3)	0.375 8(25)	C(25)	0.762 3(6)	−0.004 8(13)	0.473 8(5)
C(43)	1.023 4(16)	0.683(3)	0.444 9(25)	C(26)	0.806 8(6)	0.108 3(13)	0.492 5(5)
C(44)	0.982 2(16)	0.788(3)	0.464 6(25)	C(27)	0.780 2(6)	0.229 6(13)	0.464 7(5)
C(40′)	0.962(3)	0.836(5)	0.448(3)	C(22)	0.709 1(6)	0.237 8(13)	0.418 2(5)
C(41′)	1.010(3)	0.722(5)	0.464(3)	C(29)	0.579 0(6)	0.304 1(14)	0.271 8(6)
C(42′)	1.019(3)	0.667(5)	0.406(3)	C(30)	0.507 7(6)	0.292 9(14)	0.225 8(6)
C(43′)	0.978(3)	0.745(5)	0.353(3)	C(31)	0.443 1(6)	0.359 1(14)	0.235 2(6)
C(44′)	0.942(3)	0.850(5)	0.379(3)	C(32)	0.449 8(6)	0.436 5(14)	0.290 7(6)
C(5)	0.808 5(8)	0.203 8(14)	0.174 5(6)	C(33)	0.521 2(6)	0.447 7(14)	0.336 6(6)
C(6)	0.814 9(8)	0.068 6(14)	0.165 4(6)	C(28)	0.585 7(6)	0.381 5(14)	0.327 2(6)
C(7)	0.800 5(8)	−0.019 8(14)	0.211 2(6)	C(35)	0.657 1(8)	0.625 4(14)	0.452 5(6)
C(8)	0.779 7(8)	0.027 0(14)	0.266 0(6)	C(36)	0.635 6(8)	0.692 7(14)	0.502 3(6)
C(9)	0.773 2(8)	0.162 1(14)	0.275 0(6)	C(37)	0.614 1(8)	0.622 7(14)	0.551 3(6)
C(4)	0.787 6(8)	0.250 5(14)	0.229 3(6)	C(38)	0.614 2(8)	0.485 4(14)	0.550 5(6)
C(11)	0.646 4(8)	0.374 4(12)	0.126 6(7)	C(39)	0.635 8(8)	0.418 0(14)	0.500 8(6)
C(12)	0.575 5(8)	0.403 4(12)	0.082 9(7)	C(34)	0.657 2(8)	0.488 1(14)	0.451 7(6)

* Cyclopentadienyl atoms of lower occupancy (0.45) are indicated by primes.

Table 2. Selected bond lengths (Å) and angles (°) for complex (**2**)

W(1)–Ni(1)	2.574(3)	Ni(1)–P(1)	2.275(6)
W(1)–C(1)	1.945(23)	Ni(1)–P(2)	2.284(6)
W(1)–C(2)	1.957(21)	Ni(1)–C(2)	2.122(21)
W(1)–C(3)	1.980(19)	Ni(1)–C(3)	2.086(19)
W(1)–C(40)	2.28(4)	P(1)–C(4)	1.819(14)
W(1)–C(41)	2.26(4)	P(1)–C(10)	1.842(15)
W(1)–C(42)	2.30(4)	P(1)–C(16)	1.815(15)
W(1)–C(43)	2.36(4)	P(2)–C(22)	1.833(13)
W(1)–C(44)	2.34(4)	P(2)–C(28)	1.819(14)
W(1)–C(40′)	2.42(6)	P(2)–C(34)	1.836(15)
W(1)–C(41′)	2.34(6)	C(1)–O(1)	1.17(3)
W(1)–C(42′)	2.33(6)	C(2)–O(2)	1.16(3)
W(1)–C(43′)	2.41(6)	C(3)–O(3)	1.148(25)
W(1)–C(44′)	2.46(6)		
Ni(1)–W(1)–C(1)	86.8(7)	Ni(1)–P(1)–C(16)	111.3(5)
Ni(1)–W(1)–C(2)	53.8(6)	C(4)–P(1)–C(10)	103.8(7)
Ni(1)–W(1)–C(3)	52.6(6)	C(4)–P(1)–C(16)	102.7(7)
C(1)–W(1)–C(2)	88.3(9)	C(10)–P(1)–C(16)	104.4(7)
C(1)–W(1)–C(3)	93.9(9)	Ni(1)–P(2)–C(22)	110.1(4)
C(2)–W(1)–C(3)	106.0(8)	Ni(1)–P(2)–C(28)	118.3(5)
W(1)–Ni(1)–P(1)	121.11(17)	Ni(1)–P(2)–C(34)	116.4(5)
W(1 –Ni(1)–P(2)	128.07(16)	C(22)–P(2)–C(28)	106.1(6)
W(1)–Ni(1)–C(2)	48.1(6)	C(22)–P(2)–C(34)	102.4(6)
W(1)–Ni(1)–C(3)	48.9(5)	C(28)–P(2)–C(34)	101.9(6)
P(1)–Ni(1)–P(2)	110.79(21)	W(1)–C(1)–O(1)	175.4(20)
P(1)–Ni(1)–C(2)	101.7(6)	W(1)–C(2)–Ni(1)	78.1(8)
P(1)–Ni(1)–C(3)	113.5(6)	W(1)–C(2)–O(2)	170.3(18)
P(2)–Ni(1)–C(2)	121.5(6)	Ni(1)–C(2)–O(2)	110.8(16)
P(2)–Ni(1)–C(3)	111.8(6)	W(1)–C(3)–Ni(1)	78.5(7)
C(2)–Ni(1)–C(3)	96.7(8)	W(1)–C(3)–O(3)	167.5(17)
Ni(1)–P(1)–C(4)	116.8(5)	Ni(1)–C(3)–O(3)	111.3(15)
Ni(1)–P(1)–C(10)	116.4(5)		

distance [2.574(3) Å] is comparable to the Ni–W bonds of [Ni{W(μ-CC_6H_4Me-*p*)(μ-CO)(CO)(cp)}$_2$] and some multiple metal–metal bond character was suggested for this latter complex.[21]

Spectroscopic Studies.—I.r. spectra of complexes (**1**) and (**2**) are similar to those reported for complexes (**4**), (**5**), and (**7**),[3] showing three ν(CO) bands, two of which, at *ca.* 1 770 and 1 730 cm^{-1}, may be assigned to bridging groups. However, it must be noted that some simple ion-pair salts of $[M(CO)_3(cp)]^-$ (M = Cr, Mo, or W) show bands at frequencies approaching these low values.[15] Complex (**3**) also exhibits a very similar i.r. spectrum and this is consistent with the presence of a $Cr(CO)_3(cp)$ fragment. None of the complexes (**1**), (**2**), or (**3**) shows sharp n.m.r. resonances, although in the ^1H n.m.r. spectra broad bands assignable to Ph and cp groups can be observed; readily formed decomposition products, noted previously, can also be monitored. By using the Evans method[23] for determining magnetic susceptibility, the magnetic moment of complex (**2**) in $[^2H_6]$benzene was determined as 1.9 ± 0.2 B.M., consistent with the presence of one unpaired electron.

Complexes (**1**), (**2**), and (**3**) show e.s.r. spectra in the solid state and in solution; parameters are given in Table 3. In solution each spectrum comprises a doublet of doublets (Figure 2), arising from coupling to two inequivalent ^{31}P nuclei and g_{iso} values are greater than 2.0023, increasing with the Group 6 metal in the order Cr < Mo < W. The magnitude of $A_{iso}(^{31}P)$ corresponds to $\leqslant 2\%$ unpaired *s*-electron spin density at the P atoms[24] and this may arise both from direct delocalisation as well as by spin polarisation mechanisms from the Ni centres. There is no clear evidence for coupling to Cr, Mo, and W, although shoulders on the spectrum of complex (**2**) may tentatively be assigned to interaction with ^{183}W ($I = \frac{1}{2}$, 14.4%) giving $A_{iso}(^{183}W) < 5.0$ mT. Linewidths of resonances are quite broad, with ΔH_{pp} increasing from 1.6 to 2.4 mT in the sequence Cr < Mo < W so that metal coupling may be obscured, but it must be concluded that for $^{95/97}Mo$ or ^{53}Cr the coupling is relatively small. The unpaired electron density may be located more at the Ni centre in these complexes and the *g* values are typical of Ni^I species.[9a,b,24] However, extended-Hückel molecular orbital (EHMO) calculations on a model Ni–W

Table 3. E.s.r. parameters for complexes (**1**), (**2**), and (**3**)

	Solution[a,b]		Solid[b]				Dilute glass[b,c]		
Complex	g_{iso}	$A_{iso}(^{31}P)$	g_1	g_2	g_3	$\langle g \rangle$	$g_1/A_1(^{31}P)$	$g_2/A_2(^{31}P)$	$g_3/A_3(^{31}P)$
(**1**) $[MoNi(CO)_3(PPh_3)_2(cp)]$	2.118	7.49, 5.49	2.169	2.124	2.042	2.112	2.209 7.19, 4.80	2.074 7.53, 6.04	2.039 9.39, 5.09
(**2**) $[WNi(CO)_3(PPh_3)_2(cp)]$	2.128	7.65, 5.89	2.192	2.141	2.042	2.126	2.221 6.54, 4.44	2.087 7.5, 6.2	2.040 9.5, 5.5
(**3**) $[CrNi(CO)_3(PPh_3)_2(cp)]$	2.095	7.02, 4.74	2.130	2.098	2.032	2.087			

[a] Complexes (**1**) and (**2**) in 2-methyltetrahydrofuran, complex (**3**) in CH_2Cl_2; at *ca.* 10 °C; A_{iso} in mT, estimated error ± 0.08 mT. [b] Estimated error in g ± 0.001. [c] In 2-methyltetrahydrofuran at *ca.* -140 °C; A in mT, estimated error $\leqslant \pm 0.2$ mT.

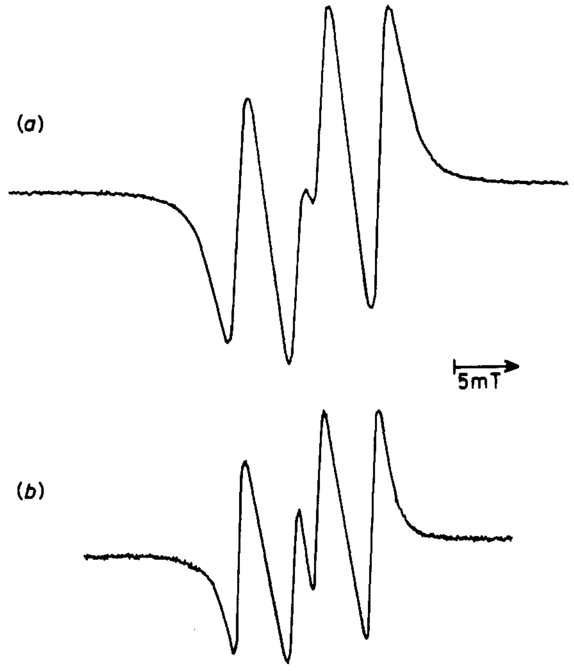


Figure 2. *X*-Band e.s.r. spectra at *ca.* 10 °C for (*a*) complex (**1**) in 2-methyltetrahydrofuran; (*b*) complex (**3**) in CH_2Cl_2

complex (see below) do support a singly occupied molecular orbital (s.o.m.o.) with a significant W component which is not inconsistent with $A_{iso}(^{183}W) \leqslant 5$ mT.[24,25]

Solid complexes show spectra typical of species with an unsymmetrical g tensor and no resolvable hyperfine structure [*e.g.* Figure 3(*a*)]. Three principal g components have average values close to g_{iso} values. Dilute samples of complexes (**1**) or (**2**) in glasses of frozen 2-methyltetrahydrofuran also exhibit features of species with three principal g values which are split anisotropically by coupling to two ^{31}P atoms [*e.g.* Figure 3(*b*)]. Analyses of these glass spectra give three g components, each associated with two $A(^{31}P)$ values (Table 3), but it must be noted that the axes of g and A tensors are unlikely to be coincident so that some of these may not be principal values.[24] Bearing this in mind, it is worth noting that the anisotropic elements of the ^{31}P coupling are all < 1.7 mT, arising mainly from dipolar coupling to the Ni centre and from unpaired *p*-electron spin density on P atoms, so that the latter must be significantly less than 8%.

EHMO Calculations of Electronic Structures.—The isolation and structural characterisation of a series of related complexes $[MM'(CO)_3(PPh_3)_2(cp)]$ (M = Mo or W; M' = Rh, Ni, or Cu) with increasing number of valence-shell electrons on changing M' in the order Rh < Ni < Cu and with an apparent concomitant decrease in metal–metal bond order prompted us to investigate the electronic structures of these species by EHMO calculations. Such calculations should indicate the extent of the heterometallic interaction and the role of the bridging CO ligands in the different systems. Model complexes $[WNi(CO)_3(PH_3)_2(cp)]$ (**8**), $[MoRh(CO)_3(PH_3)_2(cp)]$ (**9**), and $[WCu(CO)_3(PH_3)_2(cp)]$ (**10**) with idealised C_s symmetry were studied, using molecular geometries closely related to those established by *X*-ray analysis on the respective complexes (**2**), (**4**), and (**7**) (the latter in two conformations, see Experimental section for parameters).

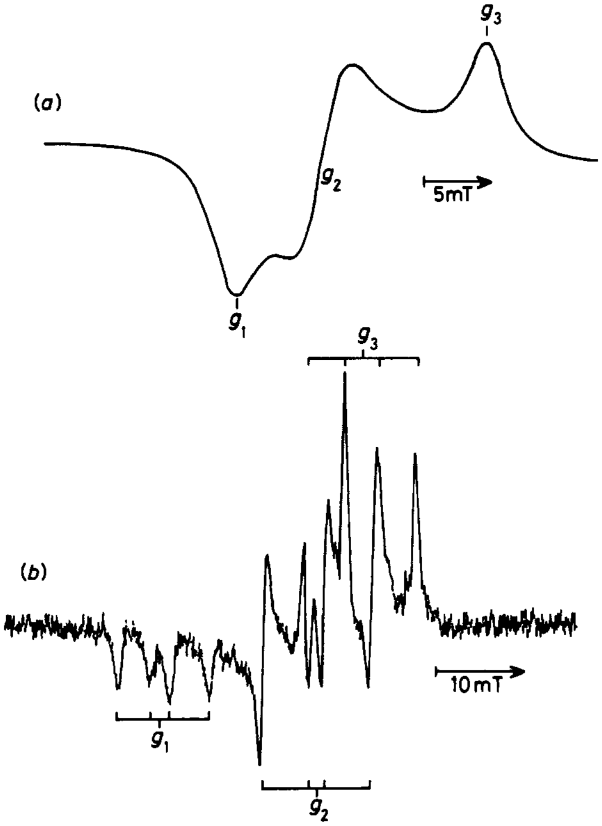


Figure 3. (*a*) E.s.r. spectrum of complex (**2**) in the solid state, *ca.* 10 °C; (*b*) e.s.r. spectrum of complex (**1**) in frozen 2-methyltetrahydrofuran at *ca.* -140 °C

Complexes (**8**)—(**10**) can be conveniently considered as a combination of the fragments $M(CO)_3(cp)$ (M = Mo or W) and $M'(PH_3)_2$ (M' = Ni, Rh, or Cu). Tricarbonyl(η^5-cyclopentadienyl)metal systems have been the subject of earlier EHMO studies.[26] The orbital energy levels for $W(CO)_3(cp)$

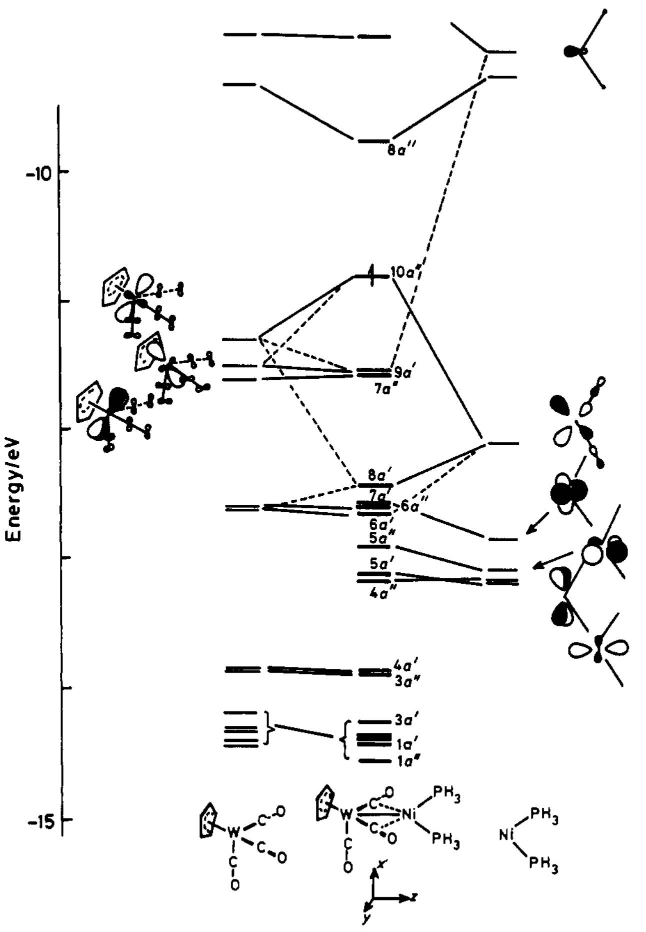


Figure 4. EHMO interaction diagram for complex (**8**) (orbital correlation derived using program FMO 39)

with the geometry relevant to complexes (**8**) and (**10**) are depicted in Figures 4 and 5. The three highest occupied orbitals, *a'*, *a'*, and *a''* in order of decreasing energy, involve W d_{xz},$d_{x^2-y^2}$; d_{z^2},d_{xz},$d_{x^2-y^2}$; and d_{xy},d_{yz} atomic orbitals, respectively, with some delocalisation on the CO ligands. Below this set of three orbitals lies a pair of W–cp bonding orbitals and, at lower energy, a pair of orbitals located primarily on the cp ligand. The lowest set of five orbitals, illustrated in the Figures all comprise <10% metal character and are W–CO or W–cp bonding, or cp localised orbitals. The $Mo(CO)_3(cp)$ fragment has a very similar electronic structure (see Figure 6). The lowest unoccupied molecular orbital (l.u.m.o.) in both systems has *a''* symmetry, is well separated from the highest occupied molecular orbital (h.o.m.o.) and mainly involves the p_z atomic orbitals of the two symmetry-related CO ligands C(2)–O(2) and C(3)–O(3) lying $\pm y$ with respect to the mirror plane.

Bent $M'L_2$ fragments have also been studied previously by EHMO calculations.[26,27] The $M'(PH_3)_2$ systems (see Figures 4—6) have a related set of five basically M' *d* orbitals falling in energy in the order M' = Rh > Ni > Cu: the composition of these orbitals is principally a hybrid involving $d_{xz} > d_{x^2-y^2} > d_{yz} > d_{xy} > d_{z^2}$. Above these orbitals are metal–ligand antibonding orbitals which play little part in the bonding of the heterobimetallic complexes except for the lowest *a'* level which has significant metal character as an *s*–*p* hybrid on M' and which may become involved in σ bonding to $M(CO)_3(cp)$.

The major orbital interactions between $W(CO)_3(cp)$ and $Ni(PH_3)_2$ that occur on formation of complex (**8**) are shown in Figure 4; dominant interactions are denoted by full lines and lesser ones by dashed lines. The π interaction involving the Ni d_{xz} hybrid orbital with the h.o.m.o. of $W(CO)_3(cp)$ generates an antibonding s.o.m.o. and a weak in-plane π-bonding orbital, 8*a'*, probably giving an overall bonding interaction for complex (**8**). The unoccupied Ni *a'* orbital interacts to a small extent with the higher $W(CO)_3(cp)$ *a'* orbitals giving a weak σ bond, 9*a'*. No other single interactions appear to contribute significantly to the bonding of (**8**). This conclusion is borne out by the reduced orbital overlap populations computed for Ni–W (0.134) and for Ni–C(2,3) (0.240) which suggest that the overall bonding is relatively weak and includes elements of direct Ni–W and of Ni–CO interactions. The net charges on the fragments $W(CO)_3(cp)$ and $Ni(PH_3)_2$ are, respectively, −0.177 and +0.177 although both metal atoms are positively charged, W (+1.18) and Ni (+0.214), with most negative charge on O atoms.

The s.o.m.o. of (**8**) is divided between the two molecular fragments with principal contributions from W d_{xy}, Ni d_{xz}, and combined orbitals of the three CO groups, and with minor amounts of P atomic orbitals [P(1): $0.15p_x + 0.13p_z$ + some *d*; P(2): $0.11\ p_x - 0.14\ p_z$ + some *d*]. Thus, only a low spin density is predicted to be located on the inequivalent P atoms which is consistent with the e.s.r. data for complex (**2**). There appears to be a substantial spin density on W (*ca.* 30%) but this is not inconsistent with the maximum value of $A_{iso}(^{183}W)$ assignable from the broadened e.s.r. spectrum for complex (**2**).[24,25]

The orbital interaction diagram for the Mo–Rh complex (**9**) is shown in Figure 6. Here the fragment orbitals lie closer in energy and stronger interactions are indicated. Overlap of the highest filled levels of the two fragments (largely Mo $d_{x^2-y^2}$,d_{xz}; and Rh d_{xz}) generate 8*a'* which is essentially a π orbital in the symmetry plane. Levels 9*a'* and 7*a'* are a corresponding pair of antibonding and bonding σ orbitals. The bridging carbonyl based l.u.m.o. of $Mo(CO)_3(cp)$ contributes *via* a three-orbital interaction with Rh d_{yz} and a Mo–CO bonding orbital to levels 6*a''* and 1*a''*; this is an out-of-plane π interaction comparable to that proposed as the main bonding in Cr–Rh and Co–Rh complexes.[28] Overall, the reduced orbital overlap populations are 0.206 (Mo–Rh), 0.358 [Rh–C(2,3)], and 0.753 [Mo–C(2,3)] so that again both direct Mo–Rh and bridging carbonyl interactions are important. Charges on fragments $Mo(CO)_3(cp)$ and $Rh(PH_3)_2$ are, respectively, −0.537 and +0.537 whereas calculated net charges on Mo and Rh are +0.433 and +0.785. [Note: the reversal of polarity of the MM' system compared to species (**8**) and (**10**).]

The orbital interaction diagram for complex (**10**) (Figure 5) is given for two conformations: (*a*) with Cu lying in the W,C(1),C(2) plane and (*b*) with the Cu–W bond at 30° to this plane. These geometries are comparable to the isomeric structures found for complex (**7**) in the solid state.[3] In either conformation there is little constructive interaction between the fragments $Cu(PH_3)_2$ and $W(CO)_3(cp)$: note the weak σ bond between the essentially Cu *sp* hybrid and a combination of the pair of highest occupied *a'* orbitals of $W(CO)_3(cp)$ appropriate to the conformation of (**10**). The reduced orbital overlap populations for conformations (*a*) and (*b*) are 0.091 or 0.133 (Cu–W) and 0.175 or 0.117 [Cu–C(2,3)], respectively; these support weak covalent interactions and the variations reflect the respective Cu–W and Cu–C bond lengths found experimentally for complex (**7**) in the two structural forms. The fragment charges on $W(CO)_3(cp)$ and $Cu(PH_3)_2$ are −0.595 and +0.595 or −0.561 and +0.561, respectively, for (*a*) or (*b*) with net charges on metals being W +0.899 or +0.856 and Cu +0.078 or +0.031. It may be concluded that ionic bonding plays an important role in these Cu–W complexes.

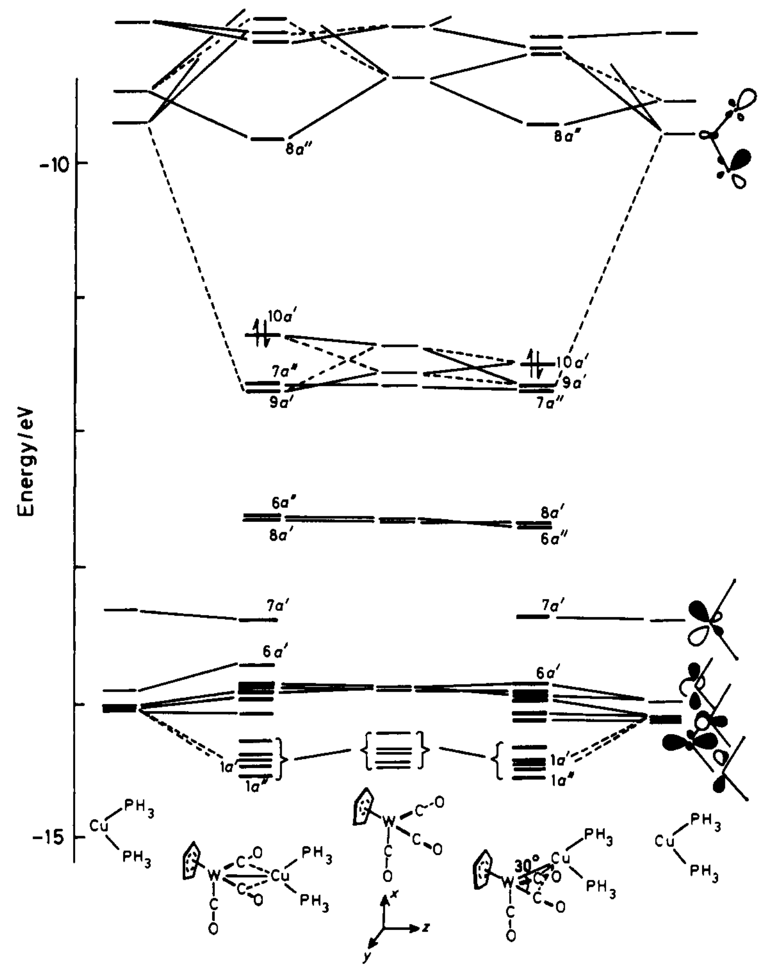


Figure 5. EHMO interaction diagram for complex (10) in two conformations (orbital correlation derived using program FMO 39)

Cyclic Voltammetric Studies.—Complexes (2), (5), and (7) have been studied by cyclic voltammetry in CH_2Cl_2 solution. [N.B. Very recently the crystal structure of (5) has been determined and is closely related to (4).[29]] Figure 7 shows representative voltammograms. The W–Ni species (2) exhibits a facile oxidation process with oxidation–reduction peaks at $E_{pa} = -0.08$, $E_{pc} = -0.22$, and $E_{\frac{1}{2}} = -0.15$ V (scan speed 0.05 V s^{-1}); the separation of these peaks is large ($\Delta E = 135$ mV) but as no compensation was made for solution *IR* drop, and since ferrocene exhibited a similar ΔE value, it may be concluded that this electrode process shows a degree of reversibility. The primary oxidation product is probably $[WNi(CO)_3(PPh_3)_2(cp)]^+$ which possesses the same number of valence electrons as complex (5) and its formation involves removal of an electron from the s.o.m.o. which is predicted by EHMO calculations to be antibonding. At higher positive potentials some irreversible oxidation processes occur for complex (2).

Complex $[WRh(CO)_3(PPh_3)_2(cp)]$ (5) is reduced in an essentially reversible process ($E_{pa} = -1.695$, $E_{pc} = -1.55$, $E_{\frac{1}{2}} = -1.62$ V, $\Delta E = 140$ mV, scan speed 0.05 V s^{-1}) at relatively low potentials; the probable product is $[WRh(CO)_3(PPh_3)_2(cp)]^-$, electronically related to complex (2) although addition of an electron to a level analogous to 10*a*′ (Figure 6), the l.u.m.o. of (9) calculated by the EHMO method, should be destabilising. In an attempt to generate $[WRh(CO)_3(PPh_3)_2(cp)]^-$ chemically by reacting (5) with Na–Hg in thf, the only identifiable product containing carbonyl groups was $[W(CO)_3(cp)]^-$. Irreversible electrochemical oxidation of complex (5) occurs on cyclic voltammetry with $E_{pa} = +0.49$ V.

The Cu–W complex (7) shows only ill defined, irreversible oxidation processes (E_{pa} +0.32, +0.60, +0.98 V) on cyclic voltammetry.

Conclusions

The new paramagnetic binuclear compounds containing a Group 6 transition metal (M) connected to nickel, structurally characterised by *X*-ray diffraction for M = W, $[(cp)(OC)W(\mu\text{-}CO)_2Ni(PPh_3)_2]$, are related to previously characterised species $[(cp)(OC)M(\mu\text{-}CO)_2M'(PPh_3)_2]$ with M′ = Rh or Cu. The Ni complexes formally contain 31 valence electrons, compared to 30 or 32 for the Rh or Cu complexes, respectively, and this is reflected in their intermediate properties with respect to structure, bonding, and aspects of reactivity.

Allowing for appropriate changes in metal radii, the crystal structures show that a lengthening of the metal–metal bond occurs in the sequence M′ = Rh < Ni < Cu and that the disposition of these metals with respect to the $M(CO)_3(cp)$ unit varies regularly, in the same order, from lying within the set of three CO ligands to an exterior position. EHMO calculations on similar model compounds indicate that both direct metal–metal and bridging CO interactions bind the two metal units and the relative strengths of these bonds are directly related to

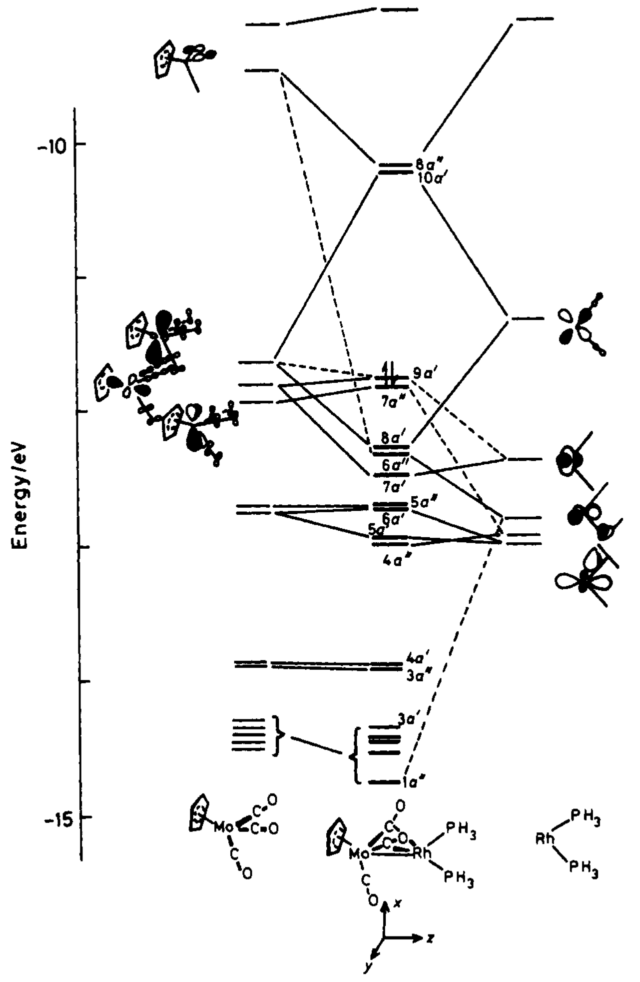


Figure 6. EHMO interaction diagram for complex (9) (orbital correlation derived using program FMO 39)

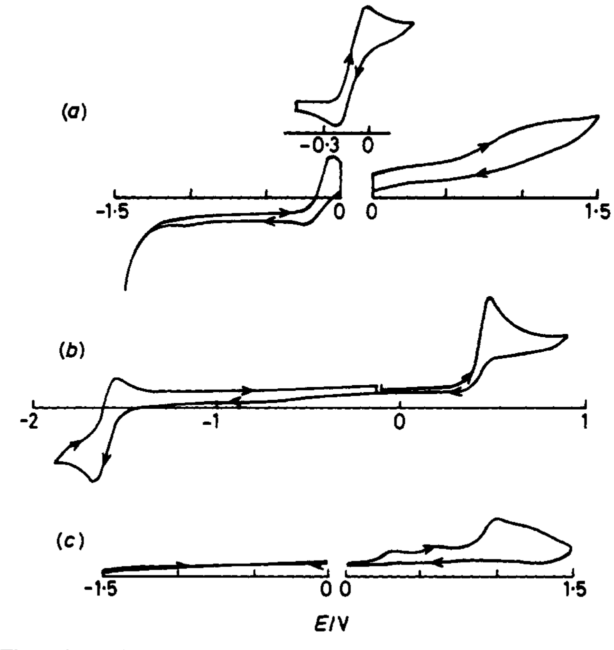


Figure 7. Cyclic voltammograms in CH_2Cl_2 solution at scan rates 0.05 V s^{-1} of: (a) complex (2); (b) complex (5); and (c) complex (7)

the crystallographically determined intermetallic distances. The M–Rh bonding shows elements of a multiple bond but the overall reduced orbital overlap population between Mo and Rh in (9) is relatively low and stronger Rh(μ-CO) interactions are indicated; weaker bonds are calculated for M′ = Ni and the unpaired electron occupies a W–Ni antibonding orbital in (8); when M′ = Cu even weaker interactions are calculated and polarity probably plays a large part in bonding. Reduction of the Rh complex (5) to a 31-electron system and oxidation of the Ni complex (2) to a 30-electron species are supported by cyclic voltammetric studies but no simple reversible redox processes have been established for Cu complexes.

The bimetallic system of the Ni complexes is readily cleaved by added ligand and the primary products appear to be a Ni^0 complex and a paramagnetic Group 6 species which dimerises or undergoes further reaction. The Rh complexes are also cleaved; photochemical scission may produce radicals but ligands may cause heterolytic cleavage or, as in the case of CO, reversible adduct formation.

Experimental

All reactions were carried out using Schlenk techniques under an atmosphere of dry, dioxygen-free, dinitrogen or under vacuum, and reagent-grade solvents were purified as described previously.[3] Starting materials $[NiCl_2(PPh_3)_2]$[30] and Na[M(CO)$_3$(cp)] (M = Cr, Mo, or W)[31] were prepared by literature methods. Known heterobimetallic complexes incorporating Rh or Cu were made as previously reported,[3] except [WCu(CO)$_3$(PPh$_3$)$_2$(cp)] (7) for which $[CuCl(PPh_3)_3]$[32] was used instead of $[\{CuCl(PPh_3)\}_4]$ as precursor: under similar reaction conditions the former gave less insoluble by-products than the latter reagent and an 83% yield of pure (7). Elemental analyses were determined principally by Analytisches Laboratorien, Elbach, West Germany, although analyses for Cr-containing products and some by-products were by Butterworth Laboratories, Teddington, U.K.

N.m.r. spectra were recorded on a Bruker WP 200SY spectrometer and the Evans method was used for susceptibility measurements.[23] I.r. spectra were run on a Perkin-Elmer 580 instrument. E.s.r. spectra were obtained on a JEOL PEI-X *X*-band spectrometer and conditions for photolytic experiments have been described previously.[33] Cyclic voltammetry was performed with a Princeton Applied 174A instrument at Pt microelectrodes in dichloromethane solutions, under argon, at concentrations *ca.* 10^{-3} mol dm^{-3} in complex and 0.1 mol dm^{-3} in NBu$^n_4$PF$_6$; no compensation was made for *IR* drop, scan rates were studied in the range 0.02—0.1 V s^{-1} and an aqueous saturated calomel electrode was employed as reference [$E_{\frac{1}{2}}$ (ferrocene–ferrocenium couple) = +0.385 V].

Preparation of [WNi(μ-CO)$_2$(CO)(PPh$_3$)$_2$(cp)] (**2**).—A solution of Na[W(CO)$_3$(cp)] (0.55 mmol) in thf (2.2 cm^3) was added to [NiCl$_2$(PPh$_3$)$_2$] (0.34 g, 0.52 mmol) and the mixture stirred at room temperature (r.t.) for 10 min. Water (15 cm^3) was then added (over 1—2 min) to give a green solid which was separated by filtration. This solid was washed well with water and subsequently with acetone until the filtrate, initially red, became virtually colourless (light green). The dark green powder was crystallised from dichloromethane–hexane at −20 °C giving dark green prisms of (**2**), which were washed with hexane and dried *in vacuo* (yield 0.25 g, 53%) (Found: C, 57.5; H, 3.9; Ni, 6.9; P, 6.6; W, 20.9. Calc. for $C_{44}H_{35}NiO_3P_2W$: C, 57.7; H, 3.85; Ni, 6.4; P, 6.8; W, 20.1%). I.r. (CH$_2$Cl$_2$): ν(CO) at 1 892, 1 769, and 1 741 cm^{-1}; (Nujol): 1 895, 1 770, and 1 730 cm^{-1}.

The red filtrate from the acetone washing was shown to contain [W$_2$(CO)$_6$(cp)$_2$] by i.r. spectroscopy.[11b] Also, after addition of hexane to this filtrate and standing for 14 d two other separable products were obtained: (*a*) red-brown crystals (*ca.* 0.01 g) of [$WCl(CO)_2(PPh_3)(cp)$][11] (Found: C, 49.0, H, 3.4. Calc. for $C_{25}H_{20}ClO_2PW$: C, 49.8; H, 3.3%) and (*b*) colourless crystals (*ca.* 0.01 g) of [$Ni(CO)_2(PPh_3)_2$][34] (Found: C, 69.9; H, 4.9. Calc. for $C_{38}H_{30}NiO_2P_2$: C, 71.4; H, 4.7%).

Preparation of [$MoNi(\mu\text{-}CO)_2(CO)(PPh_3)_2(cp)$] (**1**).—By using a similar procedure to that above, Na[$Mo(CO)_3(cp)$] (0.09 mmol) in thf (5 cm^3) and [$NiCl_2(PPh_3)_2$] (0.55 g, 0.84 mmol) gave deep green needle-like crystals of (**1**) (0.09 g, 13%). However, as this product is appreciably soluble in acetone, much is lost on washing: by employing minimum (and incomplete) washing with acetone, followed by careful crystallisation of the green solid from dichloromethane–hexane higher yields may be obtained ($\geqslant 20\%$) (Found: C, 63.7; H, 4.4; P, 7.6. Calc. for $C_{44}H_{35}MoNiO_3P_2$: C, 63.8; H, 4.3; P, 7.5%). I.r. (CH_2Cl_2): ν(CO) at 1 903, 1 778 (sh), and 1 753 cm^{-1}; (Nujol): 1 891, 1 779, and 1 739 cm^{-1}.

Several by-products are isolable from the filtrate of the acetone washing procedure: species identified by i.r. spectroscopy include [$Mo_2(CO)_6(cp)_2$], [$Mo_2(CO)_5(PPh_3)(cp)_2$],[12] and [$Ni(CO)_2(PPh_3)_2$].[34]

Reaction of Na[$Cr(CO)_3(cp)$] *with* [$NiCl_2(PPh_3)_2$].—A solution of Na[$Cr(CO)_3(cp)$] (0.6 mmol) in diglyme, ($MeOCH_2CH_2)_2O$ (1.1 cm^3), was added to [$NiCl_2(PPh_3)_2$] (0.38 g, 0.58 mmol) and the mixture stirred at r.t. for 5 min. Water (20 cm^3) was added, followed by CH_2Cl_2 (3 cm^3) and the mixture stirred for a further 3 min. The resulting green solid was filtered off, washed successively with acetone, a small amount of CH_2Cl_2 ($\leqslant 5$ cm^3) and with hexane. Attempted crystallisation of this solid led to considerable decomposition and although spectroscopic evidence suggested that this green product is largely [$CrNi(CO)_3(PPh_3)_2(cp)$] (**3**), it was not obtained pure (Found for one sample: C, 57.7; H, 4.6; Cl, 2.4; P, 6.4%). I.r. (Nujol): ν(CO) at 1 891, 1 780, and 1 738 cm^{-1}; (CH_2Cl_2): 1 918, 1778 (sh), and 1 750 cm^{-1}.

Reactions with Carbon Monoxide.—The bimetallic complex (0.02—0.1 g) dissolved in an appropriate solvent (*ca.* 10 cm^3) was stirred at r.t. under CO (1 atm). The solution was monitored periodically by i.r. spectroscopy until no further change was noted. Solid products were then isolated and separated (or partially separated) by crystallisation from CH_2Cl_2–hexane.

(*a*) Green solutions of complex (**2**) in CH_2Cl_2 reacted completely within 5 min, becoming light orange. Products identified by i.r. spectroscopy were [$Ni(CO)_3(PPh_3)$],[34] [$Ni(CO)_2(PPh_3)_2$], [$W_2(CO)_6(cp)_2$], and [$WCl(CO)_3(cp)$].

(*b*) Complex (**5**) in CH_2Cl_2, thf, or toluene reacted within *ca.* 5—10 min, the dark solution becoming light red-orange. I.r. spectra of the resulting solution all showed the absence of (**5**) and the presence of a new, strong absorption at *ca.* 1 963 cm^{-1}, accompanied by weaker ν(CO) bands in the region >1 800 cm^{-1} [*e.g.* in CH_2Cl_2: 1 963vs, 1 928 (sh), 1 888s, and 1 829s cm^{-1}]. However, on isolation of solid products, extensive reformation of (**5**) occurred, although a yellow, crystalline Rh product [ν(CO): 1 978 cm^{-1} in CH_2Cl_2] was separated from reactions in CH_2Cl_2.

Reactions with 1,2-*Bis*(*diphenylphosphino*)*ethane* (*dppe*).—(*a*) Complex (**2**) (0.116 g, 0.13 mmol) in CH_2Cl_2 (10 cm^3) and dppe (0.08 g, 0.2 mmol) were stirred at r.t. for 22 h. The green solution became brown and i.r. spectroscopy indicated the presence of [$W_2(CO)_6(cp)_2$], some unreacted (**2**), and a little [$Ni(CO)_2L_2$] (L = PPh_3 or $\frac{1}{2}$ dppe). Addition of hexane and crystallisation yielded crystals of [$W_2(CO)_6(cp)_2$] and also a buff solid containing phosphine but no carbonyl ligands.

(*b*) Complex (**5**) (0.05 g, 0.05 mmol) in CH_2Cl_2 (15 cm^3) and dppe (0.025 g, 0.06 mmol) were stirred at r.t. Within 1—2 min the solution became yellow and i.r. spectroscopy showed the absence of (**5**). After 20 min reduction in volume, addition of hexane, and cooling to −20 °C afforded a yellow crystalline solid identified as [$Rh(dppe)_2$][$W(CO)_3(cp)$]·$1.5CH_2Cl_2$ (**6**) (Found: C, 54.4; H, 4.35. Calc. $C_{61.5}H_{56}Cl_3O_3P_4RhW$: C, 54.3; H, 4.15%). I.r. (CH_2Cl_2): ν(CO) at 1 890 and 1 770 cm^{-1}. N.m.r.: ^1H (CD_2Cl_2), δ 7.37 and 7.23 (complex, Ph), 5.14 (s, C_5H_5), and 2.14 (m, CH_2CH_2) (CH_2Cl_2 also present); $^{31}P\text{-}\{^1H\}$ (CD_2Cl_2), δ 57.7 (d, $J_{Rh\text{-}P}$ 133 Hz).

X-*Ray Structure Determination of Complex* (**2**).—*Crystal data.* $C_{44}H_{35}NiO_3P_2W$, $M = 916.2$, monoclinic, space group $P2_1/c$ (no. 14), $a = 17.873(9)$, $b = 10.156(6)$, $c = 21.249(7)$ Å, $\beta = 105.05(3)°$, $U = 3\,725$ Å^3, $Z = 4$, $D_c = 1.634$ g cm^{-3}, $F(000) = 1\,820$, $\mu(Mo\text{-}K_{\bar{\alpha}}) = 39.0$ cm^{-1}; crystal dimensions 0.2 × 0.3 × 0.08 mm.

Data collection. The intensity data were collected on an Enraf–Nonius CAD4 diffractometer over the quadrant ($+h$, $+k$, l; $1 \leqslant \theta \leqslant 23°$; ω–2θ scans) using graphite-monochromated Mo-$K_{\bar{\alpha}}$ radiation (λ = 0.710 69 Å). Of 5 122 unique data measured, 2 776 had $I > \sigma(I)$ and were used in structure solution and refinement. In addition to the normal correction for Lorentz and polarisation affects, the data were also corrected for absorption (DIFABS[35]).

Structure solution. The positions of the W and Ni atoms were initially located on a Patterson map and those of the remaining non-hydrogen atoms from successive difference-Fourier maps. Full-matrix least-squares refinement, using anisotropic thermal parameters for the W, Ni, P, and O atoms and C atoms of the carbonyl groups only, reduced the discrepancy factors at convergence to $R = 0.062$ and $R' = 0.087$, where the weighting scheme $w^{-1} = \sigma^2(F) + 0.0065\ (F^2)$ gave satisfactory analyses of variance. The final difference-Fourier map was featureless apart from two peaks at *ca.* 2.1 and 1.6 e Å^{-3} situated close to the tungsten atom. The phenyl and cyclopentadienyl groups were treated as rigid hexagons (C–C 1.395 Å) and pentagons (C–C 1.42 Å) respectively with hydrogen atoms included in calculated positions (C–H 1.08 Å) and with fixed isotropic thermal parameters ($U_{iso} = 0.10$ Å^2). Rotational disorder in the cyclopentadienyl groups was modelled as a two-site occupancy which refined to relative populations of 55:45.

Computer programs used included SHELX 76[36] for structure solution and refinement, ORTEP-II[37] for plotting, and CALC[38] for incidental calculations.

Procedures for Molecular Orbital Calculations.—EHMO Calculations were carried out on the simplified model complexes (**8**)—(**10**), idealised to C_s symmetry, but with geometries based on the *X*-ray crystal structures of (**2**), (**4**),[3] and (**7**)[3] respectively, using a locally adapted version of ICON8[39] and orbital exponents for the transition-metal atoms taken from ref. 40.

The molecules were divided into fragments on the basis that the semibridging carbonyl groups remain attached to the metal to which they show a greater degree of terminal character. Analysis of the molecular orbitals of the complexes in terms of the fragment orbitals was undertaken using the program FMO.[39]

Geometrical parameters used were as follows. Complex (**8**): W–Ni 2.58, W–C(1) 1.95, W–C(2) 1.96, W–C(cp) 2.34, C(1)–O(1) 1.155, C(2)–O(2) 1.17, Ni–P 2.27 Å; Ni–W–C(1) 90, Ni–W–C(2) 52.5, C(1)–W–C(2) 90, C(2)–W–C(3) 105, and P(1)–Ni–P(2) 111°.

Complex (**9**): Mo–Rh 2.59, Mo–C(1) 1.94, Mo–C(2) 2.00, Mo–C(cp) 2.34, C(1)–O(1) 1.16, C(2)–O(2) 1.18, Rh–P 2.28 Å; Rh–Mo–C(1) 78.8, Rh–Mo–C(2) 53.73, C(1)–Mo–C(2) 90.9, C(2)–Mo–C(3) 105.35, Mo–C(1)–O(1) 175, Mo–C(2)–O(2) 162, and P(1)–Rh–P(2) 103°.

Complex (**10**): W–Cu 2.77, Cu–P 2.31 Å; P(1)–Cu–P(2) 120°; remaining geometrical parameters around the $W(CO)_3(cp)$ moiety as for (**8**).

The PH_3 groups were tetrahedral (P–H 1.42 Å; M′–P–H 109.47, H–P–H 109.47°) and the cyclopentadienyl group was a rigid pentagon (C–C 1.42, C–H 1.08 Å) for (**8**)—(**10**).

Acknowledgements

We thank the S.E.R.C. for support and also Dr. A. J. Welch, Edinburgh University, for assistance with the *X*-ray data collection.

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Received 24*th November* 1986; *Paper* 6/2263