Organometallics 1992, *11*, 2128–2139

band in the IR spectrum. The experimental evidence supports the reductive elimination of $\mathrm{Cp(CO)_2FeH}$ (eq 15)

$$\mathrm{Cp(CO)_2Fe{-}Fe(H)(SnBu_3)(CO)Cp} \xrightarrow{k_{\mathrm{slow}}} \mathrm{Cp(CO)_2Fe(H) + Cp(CO)FeSnBu_3} \quad (15)$$

rather than the alternative reductive elimination of $\mathrm{Cp(CO)_2FeSnBu_3}$ from I (cf. eq 13). Furthermore, the reductive elimination of $\mathrm{HSnBu_3}$ from I is not important (eq 14), as indicated by the fact that k_{slow} is independent of $[\mathrm{HSnBu_3}]$.[23]

Under Ar in the presence of $\mathrm{HSnBu_3}$, $\mathrm{Cp_2Fe_2(\mu\text{-}CO)_2(\eta\text{-}\eta^1,\eta^2\text{-}CO)}$ is observed via very weak peaks at 1839 and 1674 $\mathrm{cm^{-1}}$. It appears that reaction of $\mathrm{HSnBu_3}$ with $\mathrm{Cp_2Fe_2(\mu\text{-}CO)_2(\mu\text{-}\eta^1,\eta^2\text{-}CO)}$ is much slower than with $\mathrm{Cp_2Fe_2(\mu\text{-}CO)_3}$.

The kinetics of oxidative addition of $\mathrm{HSnBu_3}$ to $\mathrm{Cp_2Fe_2(\mu\text{-}CO)_3}$ are not inconsistent with an associative pathway, as suggested for the reaction of $\mathrm{Cp_2Fe_2(\mu\text{-}CO)_3}$ with other ligands.[11c,24] However, it has been demonstrated that reaction of $\mathrm{Mn_2(CO)_7L_2}$ ($\mathrm{L = PR_3}$; R = alkyl) with $\mathrm{HSnBu_3}$ involves the bridge-on–off equilibrium between the species with a semibridging CO, $\mathrm{Mn_2(CO)_6L_2(\mu\text{-}\eta^1,\eta^2\text{-}CO)}$, and a nonbridging species, $\mathrm{L(CO)_4Mn{-}Mn(CO)_3L}$; the bridging form predominantes, but only the bridge-off form reacts rapidly with $\mathrm{HSnBu_3}$.[17] The apparent rate constants, 2.5×10^6 and $3 \times 10^5\ \mathrm{M^{-1}\ s^{-1}}$, for addition of L = CO and $\mathrm{PMe_3}$, respectively, are close to that for addition of $\mathrm{HSnBu_3}$ to $\mathrm{Cp_2Fe_2(\mu\text{-}CO)_3}$. At this point it is not clear whether a bridge-on–off equilibrium precedes addition of the ligand to $\mathrm{Cp_2Fe_2(\mu\text{-}CO)_3}$. Further study of the reactions of $\mathrm{Cp_2Fe_2(\mu\text{-}CO)_3}$ with various nucleophiles is presently underway.

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[23] It was noted that diffusion processes occur on the time scale of minutes after flash photolyzing a solution in an IR cell. A portion of the solution in the cell is not exposed to the windows and thus is not photolyzed. Diffusion leads to a mixing of exposed and unexposed solution in the window area. The net effect in a difference spectrum, such as shown in Figure 8, is a decrease in absolute magnitudes of both negative and positive peaks. Thus, the observed partial recovery of 1 between 30 and 160 s after the flash does not necessarily indicate that reductive elimination of $\mathrm{HSnBu_3}$ to form $\mathrm{Cp_2Fe_2(\mu\text{-}CO)_3}$, followed by combination with CO, is occurring. In fact, such a process is expected to be unimportant under the employed reaction conditions, i.e., high $\mathrm{HSnBu_3}$ concentration and low CO concentrations in the solution.

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Reactions of the Unsaturated Species $(\eta\text{-}\mathrm{C_5Me_5})\mathrm{Ni{-}W(CO)_3}(\eta\text{-}\mathrm{C_5H_5})$ and of Its Methylene Derivative $(\eta\text{-}\mathrm{C_5Me_5})\mathrm{Ni}(\mu\text{-}\mathrm{CO})(\mu\text{-}\mathrm{CH_2})\mathrm{W(CO)_2}(\eta\text{-}\mathrm{C_5H_5})$ with Two-Electron Donors

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The unsaturated complex $(\eta\text{-}\mathrm{C_5Me_5})\mathrm{Ni{-}W(CO)_3}(\eta\text{-}\mathrm{C_5H_5})$ reacts with two-electron donor ligands or their precursors to afford compounds of generic formula $(\eta\text{-}\mathrm{C_5Me_5})\mathrm{Ni}(\mu\text{-}\mathrm{CO})(\mu\text{-}\mathrm{L})\mathrm{W(CO)L'}(\eta\text{-}\mathrm{C_5H_5})$ (L = CO; L′ = CO, $\mathrm{PMe_3}$, $\mathrm{PMe_2Ph}$, $\mathrm{P(OMe)_3}$, $\mathrm{PPh_2Cl}$, $\mathrm{PPh_2H}$. L = ^{t}BuNC, $\mathrm{CH_2}$; L′ = CO). The structure of the μ-$\mathrm{CH_2}$ species $(\eta\text{-}\mathrm{C_5Me_5})\mathrm{Ni}(\mu\text{-}\mathrm{CO})(\mu\text{-}\mathrm{CH_2})\mathrm{W(CO)_2}(\eta\text{-}\mathrm{C_5H_5})$ (2), which has been communicated (Chetcuti, M. J.; Grant, B. E.; Fanwick, P. E. *Organometallics* **1990**, *9*, 1345), has the same molecular geometry as that adopted by most of the other complexes described and is discussed in more depth here. Complex 2 crystallizes in the triclinic space group $P\bar{1}$, with $a = 8.518$ (2) Å, $b = 10.280$ (1) Å, $c = 10.719$ (1) Å, $\alpha = 89.26$ (1)°, $\beta = 87.24$ (1)°, $\gamma = 79.18$ (1)°, $V = 920.9$ (4) Å^3, $Z = 2$, and was refined to $R = 0.039$, $R_w = 0.053$. All complexes exhibit dynamic behavior on the NMR time scale that can be rationalized in light of their observed structures. The phosphine ligands $\mathrm{PMe_3}$ and $\mathrm{PPh_2H}$ displace a carbonyl ligand in $(\eta\text{-}\mathrm{C_5Me_5})\mathrm{Ni}(\mu\text{-}\mathrm{CO})(\mu\text{-}\mathrm{CH_2})\mathrm{W(CO)_2}(\eta\text{-}\mathrm{C_5H_5})$ to afford cis and trans isomers of the phosphine derivatives $(\eta\text{-}\mathrm{C_5Me_5})\mathrm{Ni}(\mu\text{-}\mathrm{CO})(\mu\text{-}\mathrm{CH_2})\mathrm{W(CO)L}(\eta\text{-}\mathrm{C_5H_5})$ (L = $\mathrm{PMe_3}$, $\mathrm{PPh_2H}$). The reaction of $(\eta\text{-}\mathrm{C_5Me_5})\mathrm{Ni{-}W(CO)_3}(\eta\text{-}\mathrm{C_5H_5})$ with $\mathrm{PPh_2Cl}$ proceeds to give the initial phosphine adduct $(\eta\text{-}\mathrm{C_5Me_5})\mathrm{Ni}(\mu\text{-}\mathrm{CO})_2\mathrm{W(CO)(PPh_2Cl)}(\eta\text{-}\mathrm{C_5H_5})$. Oxidative addition then ensues to afford the cis species $(\eta\text{-}\mathrm{C_5Me_5})\mathrm{Ni}(\mu\text{-}\mathrm{CO})(\mu\text{-}\mathrm{PPh_2})\mathrm{W(CO)Cl}(\eta\text{-}\mathrm{C_5H_5})$, which subsequently equilibrates with the trans isomer. $\mathrm{PPh_2H}$ is believed to behave similarly, but oxidative addition products are not isolable here. The behavior of the related saturated cyclopentadienylnickel complexes $(\eta\text{-}\mathrm{C_5H_5})\mathrm{(OC)Ni{-}W(CO)_3}(\eta\text{-}\mathrm{C_5H_4R})$ (R = H, Me) toward $\mathrm{PMe_3}$, $\mathrm{PPh_2H}$, and ^{t}BuNC is discussed. The syntheses of $(\eta\text{-}\mathrm{C_5Me_5})\mathrm{Ni}(\mu\text{-}\mathrm{CO})_2\mathrm{Mo(CO)(PPh_2H)}(\eta\text{-}\mathrm{C_5H_4Me})$ (Ni–Mo) and of $(\eta\text{-}\mathrm{C_5H_5})\mathrm{Ni}(\mu\text{-}{}^t\mathrm{BuNC})(\mu\text{-}\mathrm{CO})\mathrm{Mo(CO)_2}(\eta\text{-}\mathrm{C_5H_4Me})$ (Ni–Mo) are also described.

Introduction

The chemistry of homobimetallic unsaturated compounds toward 2-electron donor ligands is quite variable.[1] In some instances, simple addition to afford 1,2-addition product results. Occasionally the outcome is metal–metal bond cleavage, while, in other cases, there is no reaction at all. A few examples demonstrate that the product obtained is not always predictable. Thus, the complex $\mathrm{Re_2(\mu\text{-}CO)_3}(\eta\text{-}\mathrm{C_5Me_5})_2$ (Re≡Re) is unreactive toward

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[1] Winter, M. J. *Adv. Organomet. Chem.* **1989**, *29*, 101, and cited references.

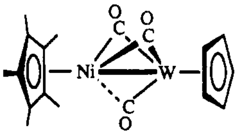
Table I. IR Data for the Complexes

complex	ν(CO), cm^{-1}	form
Cp*Ni(μ-CO)(μ-CH$_2$)W(CO)$_2$Cp (**2**)	1984 (s), 1932 (vs), 1777 (s)	hexanes
Cp*Ni(μ-CO)$_2$W(CO)(PMe$_3$)Cp (**3a**)	1891 (s), 1761 (s), 1727 (s)	THF
Cp*Ni(μ-CO)$_2$W(CO)(PMe$_2$Ph)Cp (**3b**)	1892 (s), 1762 (s), 1729 (vs), 1722 (sh)	THF
Cp*Ni(μ-CO)$_2$W(CO){P(OMe)$_3$}Cp (**3c**)	1953 (m), 1918 (s), 1908 (sh), 1773 (s), 1739 (s)	Nujol mull
	1918 (vs), 1772 (s), 1728 (s)	THF
Cp*Ni(μ-CO)$_2$W(CO)(PPh$_2$Cl)Cp (**3d**)	2030 (w), 1960 (s), 1785 (w), 1740 (s)	Nujol mull
Cp*Ni(μ-CO)$_2$W(CO)(PPh$_2$H)Cp (**3e**)	1955 (w), 1913 (s), 1762 (vs), 1726 (s)	dichloromethane
	1905 (s), 1750 (m), 1715 (s)	Nujol mull
Cp*Ni(μ-CO)$_2$Mo(CO)(PPh$_2$H)Cp′ (**3e′**)	1900 (s), 1760 (m), 1725 (s)	Nujol mull
Cp*Ni(μ-CO)(μ-CH$_2$)W(CO)(PMe$_3$)Cp (**5a, 5b**)	1878 (s), 1860 (s), 1734 (s), 1707 (s)	THF
Cp*Ni(μ-CO)(μ-CH$_2$)W(CO)(PPh$_2$H)Cp (**6a, 6b**)	1885 (s), 1710 (s), 1695 (w, sh)	Nujol mull
Cp*Ni(μ-CO)(μ-^{t}BuNC)W(CO)$_2$Cp (**7**)[a]	2165* (m), 2136* (w), 1921 (m), 1889 (s), 1803 (vs), 1779 (w), 1745 (s)	THF
CpNi(μ-CO)(μ-^{t}BuNC)W(CO)$_2$Cp′ (**7a**)[a]	2164* (w), 2122* (w), 1943 (s), 1926 (w), 1845 (m), 1803 (s), 1771 (s)	hexanes
	2149* (s), 1942 (s), 1788 (s), 1752 (vs)	Nujol mull
CpNi(μ-CO)(μ-^{t}BuNC)Mo(CO)$_2$Cp′ (**7b**)[a]	2165* (s), 2123* (w), 1946 (s), 1928 (s), 1849 (vs), 1818 (s), 1785 (s)	hexanes
	2162* (s), 1906 (s), 1829 (sh), 1809 (vs)	Nujol mull
Cp*Ni(μ-CO)(μ-PPh$_2$)WCl(CO)Cp (**8a, 8b**)	1975 (m), 1940 (s), 1785 (s), 1750 (m)	THF
	1965 (s), 1940 (vs), 1925 (sh), 1765 (vs), 1735 (s)	Nujol mull
CpNiWCp′(CO)$_3$(PMe$_3$) (**10a, 10b**)	1945 (s), 1900 (m), 1840 (m), 1790 (sh), 1770 (w), 1740 (w)	THF

[a] Absorptions marked with an asterisk are assigned to ν(NC). Other stretches are ν(CO) *or* ν(NC).

phosphine ligands, diazomethane, or alkynes,[2] and its dimanganese analogue is also relatively inert. However, the reaction of P(OEt)$_3$ with Mn$_2$(μ-CO)$_3$(η-C$_5$Me$_5$)$_2$ (Mn≡Mn) led to retrieval of *mono*nuclear Mn(CO)$_2${P(OEt)$_3$}(η-C$_5$Me$_5$) and Mn(CO){P(OEt)$_3$}$_2$(η-C$_5$Me$_5$) species.[3] The dirhodium complex Rh$_2$(μ-CO)$_2$(η-C$_5$Me$_5$)$_2$ (Rh=Rh) adds 1 equiv of either phosphine or phosphite ligands to afford the adducts Rh$_2$(μ-CO)$_2$L(η-C$_5$Me$_5$)$_2$ (Rh—Rh).[4] However, the corresponding dicobalt complex does not react with PMe$_3$; monometallic species of the type Co(η-C$_5$Me$_5$)(L—L) are obtained with the chelating diphosphine ligands Me$_2$PC$_2$H$_4$PMe$_2$ or Ph$_2$PC$_2$H$_4$PPh$_2$.[5] As a final example, the triply bonded dimolybdenum complex Mo$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$ (Mo≡Mo) adds on 2 equiv of phosphine, phosphite, or isocyanide ligands to afford 1,2-Mo$_2$(CO)$_4$L$_2$(η-C$_5$H$_5$)$_2$ (Mo—Mo), the 1,2-addition products.[6]

The recent synthesis of the mixed-metal complex (η-C$_5$Me$_5$)Ni-W(CO)$_3$(η-C$_5$H$_5$) (1)[7] in our laboratories has triggered an extensive investigation of its chemistry and reactivity. Compound 1 joins a still fairly limited set of organometallic low-valent unsaturated heterodinuclear complexes. In order to develop the chemistry of this species, an understanding of its reactivity toward simple 2-electron donor ligands was desired. This study explores the chemistry of 1 with various such donor species, including phosphine, phosphite, and isocyanide ligands. The reaction of the complex with diazomethane and the structure of the resulting bridging methylene species (η-C$_5$Me$_5$)Ni(μ-CO)(μ-CH$_2$)W(CO)$_2$(η-C$_5$H$_5$) (Ni-W) (2), which has been communicated,[8] is described in more depth here: its geometry and fluxional behavior parallel those exhibited by the ligand adducts of 1. Reactions of 1 with the diarylphosphine ligands PPh$_2$Cl and PPh$_2$H and of 2 with PMe$_3$ and PPh$_2$H are also detailed in this article. By way of contrast, the reactions of saturated analogues of 1 toward selected phosphine ligands are also presented.



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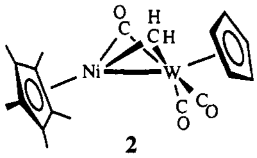

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Chart I. Naming Scheme of Compounds

1	(η-C$_5$Me$_5$)Ni–W(CO)$_3$(η-C$_5$H$_5$)
1a	(η-C$_5$Me$_5$)(OC)Ni–W(CO)$_3$(η-C$_5$H$_5$)
1b	(η-C$_5$H$_5$)(OC)Ni–W(CO)$_3$(η-C$_5$H$_4$Me)
2	(η-C$_5$Me$_5$)Ni(μ-CO)(μ-CH$_2$)W(CO)$_2$(η-C$_5$H$_5$) (Ni–W)
3a	(η-C$_5$Me$_5$)Ni(μ-CO)$_2$W(CO)(PMe$_3$)(η-C$_5$H$_5$) (Ni–W)
3a'	(η-C$_5$Me$_5$)Ni(μ-CO)$_2$W(CO)(PMe$_3$)(η-C$_5$H$_4$Me) (Ni–W)
3b	(η-C$_5$Me$_5$)Ni(μ-CO)$_2$W(CO)(PMe$_2$Ph)(η-C$_5$H$_5$) (Ni–W)
3c	(η-C$_5$Me$_5$)Ni(μ-CO)$_2$W(CO){P(OMe)$_3$}(η-C$_5$H$_5$) (Ni–W)
3d	(η-C$_5$Me$_5$)Ni(μ-CO)$_2$W(CO)(PPh$_2$Cl)(η-C$_5$H$_5$) (Ni–W)
3e	(η-C$_5$Me$_5$)Ni(μ-CO)$_2$W(CO)(PPh$_2$H)(η-C$_5$H$_5$) (Ni–W)
3e'	(η-C$_5$Me$_5$)Ni(μ-CO)$_2$Mo(CO)(PPh$_2$H)(η-C$_5$H$_4$Me) (Ni–W)
4a+	[Ni(PMe$_3$)$_2$(η-C$_5$H$_5$)]$^+$
4b+	[Ni(PMe$_2$Ph)$_2$(η-C$_5$H$_5$)]$^+$
4e+	[Ni(PPh$_2$H)$_2$(η-C$_5$Me$_5$)]$^+$
5a *cis*	(η-C$_5$Me$_5$)Ni(μ-CO)(μ-CH$_2$)W(CO)(PMe$_3$)(η-C$_5$H$_5$) (Ni–W)
5b *trans*	(η-C$_5$Me$_5$)Ni(μ-CO)(μ-CH$_2$)W(CO)(PMe$_3$)(η-C$_5$H$_5$) (Ni–W)
6a *cis*	(η-C$_5$Me$_5$)Ni(μ-CO)(μ-CH$_2$)W(CO)(PPh$_2$H)(η-C$_5$H$_5$) (Ni–W)
6b *trans*	(η-C$_5$Me$_5$)Ni(μ-CO)(μ-CH$_2$)W(CO)(PPh$_2$H)(η-C$_5$H$_5$) (Ni–W)
7	(η-C$_5$Me$_5$)Ni(μ–CO)(μ-^{t}BuNC)W(CO)$_2$(η-C$_5$H$_5$) (Ni–W)
7a	(η-C$_5$H$_5$)Ni(μ–CO)(μ-^{t}BuNC)W(CO)$_2$(η-C$_5$H$_4$Me) (Ni–W)
7b	(η-C$_5$H$_5$)Ni(μ–CO)(μ-^{t}BuNC)Mo(CO)$_2$(η-C$_5$H$_4$Me) (Ni–Mo)
8a *cis*	(η-C$_5$Me$_5$)Ni(μ-CO)(μ-PPh$_2$)W(CO)Cl(η-C$_5$H$_5$) (Ni–W)
8b *trans*	(η-C$_5$Me$_5$)Ni(μ-CO)(μ-PPh$_2$)W(CO)Cl(η-C$_5$H$_5$) (Ni–W)
9	NiW(CO)$_2$(μ-PPh$_2$)H(η-C$_5$H$_5$)(η-C$_5$Me$_5$) (Ni–W)
10a	(η-C$_5$H$_5$)(CO)Ni–W(CO)$_2$(PMe$_3$)(η-C$_5$H$_4$Me)
10b	(η-C$_5$H$_5$)(PMe$_3$)Ni–W(CO)$_3$(η-C$_5$H$_4$Me)

Results and Discussion

1. Reaction of (η-C$_5$Me$_5$)Ni-W(CO)$_3$(η-C$_5$H$_5$) (1) with Terminal Ligands. (a) Addition of PMe$_3$ and PMe$_2$Ph to 1 and the Attempted Addition of PPh$_3$. When a

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Table II. ^{1}H NMR Data for the Reported Complexes[a]

	$\mathrm{Ni(C_5}\mathit{Me}_5)$	$\mathrm{W(C_5}\mathit{H}_5)$	L or L′
2[b]	1.94	4.43	4.08 (2 H, CH_2)
3a	1.71	5.07 (d, J_{PH} = 1.2)	1.63 (d, 9 H, PMe_3, J_{PH} = 9.7)
3b	1.76	4.76 (d, J_{PH} = 1.2)	7.72–7.44 (m, 5 H, PPh); 1.97 (d, 6 H, PMe_2, J_{PH} = 9.6)
3c	1.70	5.11 (d, J_{PH} = 0.5)	3.67 (d, 9 H, $P(OMe)_3$, J_{PH} = 11.2)
3d	1.77 (d, J_{PH} = 1.8)	5.56	7.95–7.35 (m, 10 H, PPh_2)
3e[c]	1.71	4.81	7.48–7.36 (m, 10 H, PPh_2); 7.42 (d, PH, J_{PH} = 381)
4e$^+$[d]	1.56 (t, J_{PH} = 2.8)		7.52–7.26 (m, 20 H, Ph); 6.46 (d, PH, J_{PH} = 382)
5a	1.76	5.15 (d, J_{PH} = 1.6)	4.84 (dd, H, CH, J_{PH} = 9.7, J_{HH} = 4.8); 4.44 (dd, H, CH, J_{PH} = 21.3, J_{HH} = 4.8); 1.56 (d, 9 H, PMe_3, J_{PH} = 9.5)
5b	1.74	5.15 (d, J_{PH} = 1.6)	4.64 (d, 2 H, CH_2, J_{PH} = 3.3); 1.55 (d, 9 H, PMe_3, J_{PH} = 9.5)
6a[c]	1.75	4.83	7.54–7.30 (m, Ph, overlaps with **6b**); 6.90 (d, PH, J_{PH} = 378); 4.22 (dd, H, CH, J_{PH} = 48.2, J_{HH} = 3.7); 4.14 (dd, H, CH, J_{PH} = 62.4, J_{HH} = 3.7)
6b[c]	1.64	4.66 (d, J_{PH} = 1.1)	7.54–7.30 (m, Ph, overlaps with **6a**); 7.30 (d, PH, J_{PH} = 385); 3.92 (2 H, CH_2)
7[e]	1.71	5.23	1.43 (9 H, ^{t}Bu)
8a	1.81 (d, J_{PH} = 1.4)	5.158[f]	7.86–7.77; 7.45–7.25 (m, Ph, overlap with **8b**)
8b	1.65 (d, J_{PH} = 1.6)	5.163 (d, J_{PH} = 1.8)	7.86–7.77; 7.45–7.25 (m, Ph, overlap with **8a**)

	$\mathrm{C_5}\mathit{H}_5$	$\mathrm{C_5}\mathit{H}_4\mathrm{Me}$	Me	L
3e′	1.73[g]	4.70 (m, 2 H); 4.76 (m, 2 H)	2.08	7.65–7.37 (m, 10 H, Ph); 7.0 (H, PH)
4a$^+$[h]	5.61	4.89 (m, 2 H); 4.83 (m, 2 H)	2.06	1.64 (m, 18 H, PMe_3)
4b$^+$[h]	5.77	4.89 (m, 2 H); 4.83 (m, 2 H)	2.06	7.68–7.42 (m, 10 H, Ph); 1.63 (m, 12 H, PMe_2)
7a	5.17	5.10–5.05 (m, 4 H)	1.98	1.57 (9 H, ^{t}Bu)
7b	5.28	5.13 (m, 2 H); 5.07 (m, 2 H)	1.95	1.47 (9 H, ^{t}Bu)
10a	5.10	5.06 (m, 2 H); 4.88 (m, 2 H)	1.87	1.68 (d, 9 H, PMe_3, J_{PH} = 9.7)
10b	5.34	5.30 (m, 2 H); 5.23 (m, 2 H)	2.15	1.30 (d, 9 H, PMe_3, J_{PH} = 10.3)

[a] δ, ppm. In acetone-d_6 unless otherwise stated; coupling constants in hertz. [b] Benzene-d_6. [c] Dichloromethane-d_2. [d] With iodide as the counterion. [e] Chloroform-d_1. [f] In chloroform-d_1, δ = 5.04 (d, J_{PH} = 0.2) ppm. [g] $\mathrm{C_5}\mathit{Me}_5$. [h] Run with $[W(CO)_3(\eta\text{-}C_5H_4Me)]^-$ as the counterion.

Table III. ^{13}C NMR Data for the Reported Complexes[a]

	CO	$\mathit{C}_5\mathrm{Me}_5$	$\mathit{C}_5\mathrm{H}_5$	$\mathrm{C}_5\mathit{Me}_5$	L
2	238.1 (2 C); 217	100.5	90.3	8.9	57.2 (CH_2, J_{WC} = 38)
3a	253.9; 245.2 (d, 2 C, J_{PC} = 15)	99.6	90.8	9.1	19.4 (d, PMe_3, J_{PC} = 32)
3b	252.1; 244.7 (d, 2 C, J_{PC} = 15)	99.4	91.6	9.0	140.1 [d, C(1) Ph, J_{PC} = 44.2]; 130.4 [C(4) Ph, J_{PC} = 1]; 130.3 (d, 2 C Ph, J_{PC} = 8.4); 129.3 (d, 2 C Ph, J_{PC} = 9.1); 18.1 (d, PMe_3, J_{PC} = 32.8)
3c	not observed	99.7	90.9	9.0	53.0 [d, $P(OMe)_3$, J_{PC} = 6.2]
3e[b]	252.1; 242.2 (d, 2 C, J_{PC} = 12)	98.4	90.3	8.4	132.1 (d, 2 C Ph, J_{PC} = 9); 130.3 [C(4) Ph]; 128.6 (d, 2 C Ph, J_{PC} = 9)
4e$^+$I$^-$[c]		105.9		9.9	133.0 ("t", 2 C Ph, "J_{PC}" = 6); 131.2 [C(4) Ph]; 129.0 ("t", 2 C Ph, "J_{PC}" = 5)
5a[c]	not observed	99.6	90.1	9.7	87.4 (d, CH_2, J_{PC} = 4.4); 19.1 (d, PMe_3, J_{PC} = 32.0)
5b[c]	250.9 (d, 2 C, J_{PC} = 17)	99.5	89.7	9.7	85.5 (d, CH_2, J_{PC} = 19.9); 18.6 (d, PMe_3, J_{PC} = 33.3)
6a[b]	264.2 (d, J_{PC} = 10); 224.4 (d, J_{PC} = 9)	98.9	88.4	9.4	133.4 [d, C(1) Ph, J_{PC} = 44]; 133.3 [d, C(1) Ph, J_{PC} = 40]; 132.8; 132.6 and 128.8 (all d, all 2 C Ph, J_{PC} = 9); 130.10 [C(4) Ph]; 130.05 [d, C(4) Ph, J_{PC} = 2]; 128.7 (d, 2 C Ph, J_{PC} = 8); 70.2 (d, CH_2, J_{WC} = 51, J_{PC} = 14)
6b[b]	251.3 (d, J_{PC} = 9)	99.0	88.0	9.1	132.0 [d, C(1) Ph, J_{PC} = 32]; 132.5 (d, 2 C Ph, J_{PC} = 10); 130.0 [C(4) Ph]; 128.6 (d, 2 C Ph, J_{PC} = 9); 56.0 (d, CH_2, J_{PC} = 5)
7[c]	235.8	104.3	88.6	9.7	30.7 (Me_3CNC)
8a[c]	253.9; 218.5 (d, 2 C, J_{PC} = 12)	101.9	90.4	8.9	140.8 [d, C(1) Ph, J_{PC} = 45]; 135.0 (d, 2 C Ph, J_{PC} = 8); 132.6 (d, 2 C Ph, J_{PC} = 10); 127.9 (d, 2 C Ph, J_{PC} = 10); 127.6 (d, 2 C Ph, J_{PC} = 10); 129.3 [C(4) Ph]; 128.4 [d, C(4) Ph, J_{PC} = 2]
8b[c]	245.5 (d, J_{PC} = 13)	103.4	92.4	8.7	138.4 [d, C(1) Ph, J_{PC} = 43]; 133.3 (d, 2 C Ph, J_{PC} = 10); 129.2 [d, C(4) Ph, J_{PC} = 2]; 128.2 (d, 2 C Ph, J_{PC} = 11)

	CO	$\mathit{C}_5\mathrm{H}_4\mathrm{Me}$	$\mathit{C}_5\mathrm{H}_5$	$\mathrm{C}_5\mathrm{H}_4\mathit{Me}$	L
3a′	257.0 (J_{WC} = 77.5); 247.3 (d, 2 C, J_{PC} = 15, J_{WC} = 121)	107.3 [C(1)]; 93.2; 86.4	98.8;[d] 8.9	12.6	18.7 (d, PMe_3, J_{PC} = 32)
4a$^+$[e]	227 (J_{WC} = 200)	103.9 [*C(1)*]; 84.3; 83.5	94.0	14.6	18.6 ("t", PMe_3, "J_{PC}" = 17)
7a	not observed	108.4 [C(1)]; 92.4; 89.1	93.7	13.3	59.5 (br, Me_3C); 30.8 (Me_3C)
7b	244.8	109.8 [C(1)]; 93.4; 91.1	93.5	14.0	59.1 (br, Me_3C); 30.5 (Me_3C)
10a	230.9	108.2 [C(1)]; 93.3; 87.2	94.3	12.6	18.3 (d, PMe_3, J_{PC} = 34)
10b	229.7	107.9 [C(1)]; 91.2; 89.2	94.0	14.3	17.0 (d, PMe_3, J_{PC} = 29)

[a] δ, ppm. In acetone-d_6 unless otherwise stated; coupling constants in hertz. [b] Dichloromethane-d_2. [c] Chloroform-d_1. [d] $\mathit{C}_5\mathrm{Me}_5$ and $\mathrm{C}_5\mathit{Me}_5$, respectively. [e] Values in italics are for the $[W(CO)_3(\eta\text{-}C_5H_4Me)]^-$ anion.

hexane solution of **1** was treated with 1 equiv of trimethylphosphine at −78 °C, the deep blue color of **1** was discharged immediately, and a red-brown solution developed. Workup and subsequent crystallization led to the isolation of yellow-brown crystals of a new product (**3a**) in good yield. When **1** was treated with excess PMe_3, or when **3a** was treated with additional PMe_3, no further reaction ensued.

The structure of **3a** can be deduced from its spectroscopic data (Tables I–IV). Frequencies of the three absorptions noted in the ν(CO) region of the IR spectrum corresponded to one terminal and two bridging carbonyl groups [ν(CO) = 1891, 1761, and 1727 cm^{-1}, respectively]. Resonances for $\eta\text{-}C_5Me_5$, $\eta\text{-}C_5H_5$, and PMe_3 groups were noted in the ^{1}H NMR spectrum of **3a**: signal integration indicated that these ligands were present in a 1:1:1 ratio.

Table IV. ^{31}P NMR Data[a]

	δ, ppm	J_{WP}		δ, ppm	J_{WP}
3a	−32.7	219	**4e$^+$I$^-$**[c]	20	0
3b	−25.2	218	**5a**[b]	−22.5	226
3c	138.3	395	**5b**[b]	−23.2	237
3d[b,c]	31	145	**8a**[c]	75.3	197
3e[d]	−13	210	**8b**[c]	45.0	199
4a$^+$	−4	0	**10a**[e]	−39.9	211
4b$^+$	7	0	**10b**[e]	6.7	0

[a] In dichloromethane/acetone-d_6 unless otherwise stated. [b] At −20 or −25 °C. [c] Chloroform-d_1. [d] At −40 °C. [e] Acetone-d_6.

The η-C_5*H*$_5$ resonance was coupled to the ^{31}P nucleus and appeared as a doublet, suggesting that the PMe$_3$ ligand was ligated to the tungsten atom. (The η-C_5*Me*$_5$ signal was not split.) The ^{31}P{^{1}H} NMR spectrum (Table IV) corroborated this as significant ^{183}W–^{31}P coupling was observed for the single peak in the ^{31}P NMR spectrum (J_{WP} = 219 Hz). These data suggest that **3a** may be formulated as the heterodinuclear complex (η-C_5Me_5)Ni(μ-CO)$_2$W(CO)(PMe$_3$)(η-C_5H_5) (Ni–W).

The chemical shifts of the carbonyl ligands in the ^{13}C NMR spectrum of **3a** are anomalous in light of the structure of the complex. To the extent that terminal carbonyl groups typically resonate at chemical shifts that are *upfield* of bridging carbonyl ligands, the observed intensity ratio of the two signals is contrary to that expected for a species that contains two bridging and a terminal carbonyl group. The signals, which resonate at δ 253.9 (1 C) and 245.2 (2 C) ppm, tend to suggest the complementary carbonyl ligand geometry of one bridging and two terminal CO groups. A ^{13}C NMR spectrum of the analogous (but far more soluble) methylcyclopentadienyl-tungsten complex (η-C_5Me_5)Ni(μ-CO)$_2$W(CO)(PMe$_3$)(η-C_5H_4Me) (Ni–W) (**3a′**)[9] was obtained at −70 °C. The carbonyl region of the ^{13}C NMR spectrum of this species is very similar to the ambient temperature spectrum of **3a**.

The reaction with PMe$_2$Ph proceeded in similar fashion and resulted in the formation of the monophosphine adduct (η-C_5Me_5)Ni(μ-CO)$_2$W(CO)(PMe$_2$Ph)(η-C_5H_5) (**3b**). This species is believed to have a structure similar to that of **3a**, with a tungsten-bound PMe$_2$Ph ligand and two bridging and one terminal carbonyl ligands. The chemical shift "anomaly" manifested by **3a** and **3a′** for the ^{13}C NMR shifts of the carbonyl ligands is also displayed in **3b**.

Only one signal was noted for the P*Me*$_2$Ph protons (Table II). This signal, which was split by ^{31}P–^{1}H coupling, indicated that an effective plane of symmetry bisected the molecule. While the ^{13}C NMR data and the equivalent P*Me*$_2$Ph groups are incompatible with the specified static structure, they can be explained by proposing dynamic behavior on the ^{1}H NMR time scale as will be discussed shortly. The formation of these compounds is represented by eq 1.

$$\underset{\textbf{1}}{(\eta\text{-}C_5Me_5)Ni\text{–}W(CO)_3(\eta\text{-}C_5H_5)} + L \rightarrow$$

$$(\eta\text{-}C_5Me_5)Ni(\mu\text{-}CO)_2W(CO)L(\eta\text{-}C_5H_5) \quad (1)$$

$$\textbf{3a}, L = PMe_3$$

$$\textbf{3b}, L = PMe_2Ph$$

Complex **3b** is not stable indefinitely in solution. Acetone-d_6 solutions of **3b** decomposed over a 7-day period to give a complex mixture of products that was not separated. ^{1}H NMR spectroscopy (coupled with other results presented later in this paper) suggested that [Ni(PMe$_2$Ph)$_2$(η-C_5Me_5)]$^+$ was one of these decomposition species. The counteranion to this species initially is likely to be [W(CO)$_3$(η-C_5H_5)]$^-$, but this anion undergoes further attack by fortuitous water or oxygen to give decomposition species.

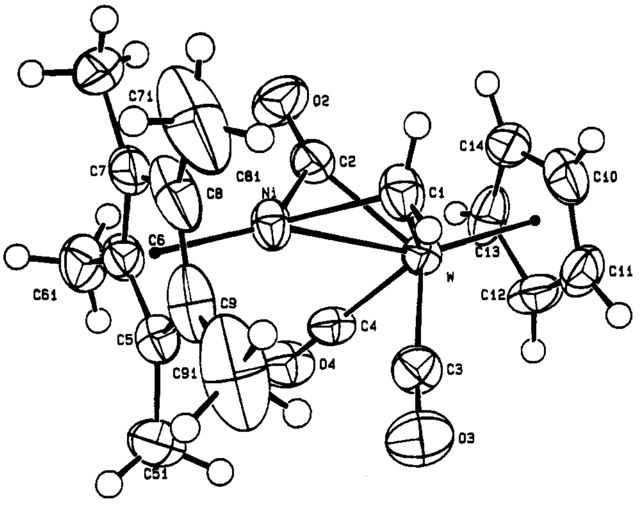
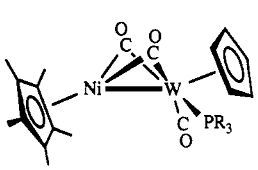


Figure 1. ORTEP plot of **2**.

Triphenylphosphine did not react with **1**—solutions of the unsaturated heterobimetallic species can be recovered unchanged when treated with excess PPh$_3$. Presumably, the large cone angle of this ligand[10] bars the formation of a stable triphenylphosphine adduct.

(b) Reaction of 1 with P(OMe)$_3$. Trimethyl phosphite also reacted with **1**. The geometry of the resultant (η-C_5Me_5)Ni(μ-CO)$_2$W(CO){P(OMe)$_3$}(η-C_5H_5) adduct (**3c**), deduced from its spectroscopic signature, resembled those of the trialkylphosphine adducts. The large tungsten–phosphorus coupling constant (J_{WP} = 395 Hz) indicates a tungsten-bound trimethyl phosphite ligand is present. However, the three ν(CO) stretches exhibited by **3c** are all shifted to higher energies, reflecting the greater π-acidity of trialkylphosphite vs trialkylphosphine ligands. The structures of **3a–c**, and of related **3d** and **3e** (vide infra) are shown. The geometry of these molecules is based on that of **2**, a discussion of which follows.



3a, PR$_3$ = PMe$_3$
3b, PR$_3$ = PMe$_2$Ph
3c, PR$_3$ = P(OMe)$_3$
3d, PR$_3$ = PPh$_2$Cl
3e, PR$_3$ = PPh$_2$H

2. Reaction of 1 with Diazomethane. (a) Synthesis and Structure of the Bridging Methylene Complex (η-C_5Me_5)Ni(μ-CO)(μ-CH$_2$)W(CO)$_2$(η-C_5H_5) (Ni–W) (2). Diazomethane reacts with a cold ethereal solution of **1** at −78 °C, liberating nitrogen to form **2** in high yield (eq 2).[8]

$$\underset{\textbf{1}}{(\eta\text{-}C_5Me_5)Ni\text{–}W(CO)_3(\eta\text{-}C_5H_5)} + CH_2N_2 \rightarrow$$

$$\underset{\textbf{2}}{(\eta\text{-}C_5Me_5)Ni(\mu\text{-}CO)(\mu\text{-}CH_2)W(CO)_2(\eta\text{-}C_5H_5)} + N_2 \quad (2)$$

2 and its Ni–Mo analogue are the first methylene complexes of nickel isolated. Their chemistry toward unsaturated hydrocarbon ligands is under investigation, as these reactions may have a bearing on models for homogeneous Fischer–Tropsch catalysis.[11] Full details of the structure

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[9] This species was prepared in similar fashion by addition of PMe$_3$ to (η-C_5Me_5)Ni–W(CO)$_3$(η-C_5H_4Me). The ^{13}C NMR spectrum of (η-C_5Me_5)Ni(μ-CO)$_2$W(CO)(PMe$_3$)(η-C_5H_4Me) (**3a′**) is consistent with this formulation, but **3a′** was not further characterized.

[10] The cone angle of PPh$_3$ is estimated at 145°: Tollman, C. A. *Chem. Rev.* **1977**, *77*, 313.

Table V. Crystal Data and Data Collection Parameters

formula	$WNiO_3C_{19}H_{22}$
fw	540.95
space group	$P\bar{1}$ (No. 2)
a, Å	8.518 (2)
b, Å	10.280 (1)
c, Å	10.719 (1)
α, deg	89.26 (1)
β, deg	87.24 (1)
γ, deg	79.18 (1)
V, Å^3	920.9 (4)
Z	2
d_{calc}, g cm^{-3}	1.951
cryst dimens, mm	0.63 × 0.52 × 0.47
temp, °C	20.
radiatn (wavelength)	Mo Kα (0.71073 Å)
monochromator	graphite
linear abs coeff, cm^{-1}	74.17
abs correctn applied	empirical[a]
transm factors: min, max	0.50, 1.00
diffractometer	Enraf-Nonius CAD4
scan method	ω–2θ
hkl limits	−10 to +11, −13 to +13, 0–13
2θ range, deg	4.00–55.00
scan width, deg	0.80 + 0.35 tan θ
take-off angle, deg	3.15
programs used	Enraf-Nonius SDP
F_{000}	524.0
p-factor used in weighting	0.040
no. of data collected	4202
no. of unique data	4202
data with $I > 3.0\sigma(I)$	3675
no. of variables	217
largest shift/esd in final cycle	0.10
R	0.039
R_w	0.053
goodness of fit	1.935

[a] Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *A39*, 158.

Table VI. Positional Parameters and Their Estimated Standard Deviations[a]

Atom	*x*	*y*	*z*	*B*, Å^2
W	0.22628 (3)	0.45960 (2)	0.22409 (2)	2.737 (4)
Ni	0.2694 (1)	0.69763 (8)	0.25469 (9)	3.12 (2)
O(2)	0.2398 (8)	0.6527 (6)	−0.0042 (5)	5.0 (1)
O(3)	0.1894 (9)	0.4983 (7)	0.5144 (6)	5.6 (2)
O(4)	−0.1334 (7)	0.5989 (7)	0.2264 (6)	5.0 (1)
C(1)	0.4318 (9)	0.5445 (7)	0.2730 (8)	3.8 (1)
C(2)	0.2411 (9)	0.6142 (7)	0.1007 (7)	3.5 (1)
C(3)	0.2008 (9)	0.4896 (8)	0.4101 (7)	3.6 (1)
C(4)	−0.0034 (8)	0.5503 (7)	0.2264 (7)	3.3 (1)
C(5)	0.1142 (8)	0.8428 (6)	0.3791 (7)	3.2 (1)
C(6)	0.1134 (8)	0.8844 (6)	0.2506 (7)	3.2 (1)
C(7)	0.2715 (9)	0.8941 (6)	0.2087 (9)	4.1 (2)
C(8)	0.3721 (9)	0.8522 (7)	0.308 (1)	5.8 (2)
C(9)	0.274 (1)	0.8232 (7)	0.4155 (8)	4.7 (2)
C(10)	0.414 (1)	0.2721 (8)	0.1659 (9)	4.6 (2)
C(11)	0.303 (1)	0.2329 (8)	0.2526 (8)	4.3 (2)
C(12)	0.155 (1)	0.2569 (7)	0.2048 (7)	4.3 (2)
C(13)	0.170 (1)	0.3142 (7)	0.0809 (8)	4.4 (2)
C(14)	0.334 (1)	0.3207 (8)	0.0606 (8)	4.5 (2)
C(51)	−0.031 (1)	0.8282 (9)	0.4586 (9)	4.9 (2)
C(61)	−0.030 (1)	0.9207 (9)	0.1760 (9)	4.7 (2)
C(71)	0.321 (1)	0.9384 (8)	0.080 (1)	6.8 (2)
C(81)	0.545 (1)	0.855 (1)	0.312 (2)	10.0 (4)
C(91)	0.325 (2)	0.784 (1)	0.544 (1)	9.0 (3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as follows: $(^4/_3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Table VII. Key Bond Distances (Å)[a]

W–Ni	2.5689 (6)	W–C(1)	2.185 (5)
W–C(2)	2.073 (6)	W–C(3)	2.017 (5)
W–C(4)	2.002 (5)	Ni–C(1)	1.906 (5)
Ni–C(2)	1.916 (6)		
W–C(Cp*)	1.426 (mean)	Ni–C(Cp)	1.407 (mean)
C(Cp*)–C(Me)	1.492 (mean)		

[a] Estimated standard deviations in parentheses.

Table VIII. Key Bond Angles (deg)[a]

Ni–W–C(1)	46.4 (1)	Ni–W–C(2)	47.3 (1)
Ni–W–C(3)	74.9 (2)	Ni–W–C(4)	82.0 (2)
C(1)–W–C(2)	72.7 (2)	C(1)–W–C(3)	74.4 (2)
C(1)–W–C(4)	127.3 (2)	C(2)–W–C(3)	121.3 (2)
C(2)–W–C(4)	79.6 (2)	C(3)–W–C(4)	83.7 (2)
W–Ni–C(1)	56.1 (2)	W–Ni–C(2)	52.6 (2)
C(1)–Ni–C(2)	82.8 (2)	W–C(1)–Ni	77.5 (2)
W–C(2)–Ni	80.1 (2)	W–C(2)–O(2)	148.0 (4)
Ni–C(2)–O(2)	131.9 (4)	W–C(3)–O(3)	175.8 (5)
W–C(4)–O(4)	178.5 (5)		

[a] Estimated standard deviations in parentheses.

and fluxionality of **2** are presented as these discussions impact the bulk of the complexes discussed here.

The structure of **2** was established by a single-crystal X-ray diffraction study. Tables of crystal data and data collection parameters, crystal coordinates, bond lengths, and bond angles of key atoms are collected in Tables V–VIII respectively. The molecular structure of **2** is shown in an ORTEP plot (Figure 1).

2 contains a somewhat short Ni–W single bond [Ni–W = 2.5689 (6) Å] that is spanned by μ-CH_2 and μ-CO ligands.[12] Both M–CH_2 bond lengths fall in ranges observed for respective metal–alkyl complexes. The bridging ligands are in a cisoid arrangement, resulting in a butterfly core geometry for the carbon atoms of these ligands and the nickel and tungsten atoms. There is no intramolecular mirror plane, and the dihedral angle subtended by the Ni–C(O)–W and the Ni–C(H_2)–W planes is only 109°. The two dienyl ligands are mutually trans; the η-C_5H_5 ring is syn to the bridging ligands, but the more sterically demanding η-C_5Me_5 group and the terminal CO groups are in an anti position relative to them.

Spectroscopic data for **2**, especially the IR (Table I) and NMR data (tables II and III), are intriguing. The IR data imply that there are a terminal and two bridging carbonyl ligands present. In addition to the surprisingly upfield chemical shift for the CH_2 nuclei in both ^{1}H and ^{13}C NMR spectra, which has been commented on,[8] the CH_2 protons of **2** (and of its Ni–Mo analogue) resonate as a singlet in their ^{1}H NMR spectra. However, the X-ray diffraction study clearly indicates that the molecule lacks the plane of symmetry required for the chemical equivalency of these protons, and an AB-type multiplet is "expected" from the molecular solid-state geometry.

The CO region of the low-temperature ^{13}C NMR spectrum revealed two resonances at δ 238 and 217 ppm (in a 2:1 ratio, respectively). The larger signal appeared at a chemical shift that was ~20 ppm downfield of the smaller signal. To the extent that terminal carbonyl groups typically resonate at chemical shifts that are *upfield* of bridging carbonyl ligands, the observed intensity ratio of the two signals is contrary to that expected for a species that contains one bridging and two terminal carbonyl groups and is inconsistent with the established solid-state structure of **2**. The relative intensities noted for the two

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(11) Chetcuti, M. J.; Grant, B. E.; Fanwick, P. E. *Organometallics* **1991**, *10*, 3003. For a discussion of the role of methylene complexes in the Fischer–Tropsch reaction, see: Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 159, and cited references.

(12) For a listing of Ni–W bond lengths, see: Chetcuti, M. J.; Fanwick, P. E.; Gordon, J. C.; Green, K. A.; Morgenstern, D. *Organometallics* **1989**, *8*, 1790.

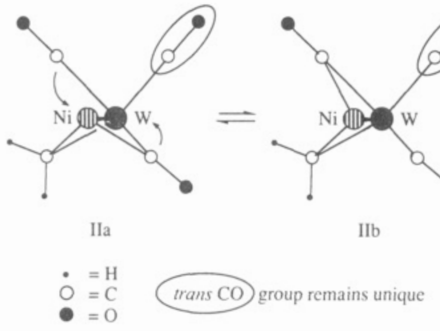


Figure 2. Molecular plot of **2**.

carbonyl ligands in the ^{13}C NMR spectrum resemble those "expected", but not seen, for **3a** and **3b**.

(b) Spectroscopic Data and Dynamic Behavior of 2. Evidently, in solution **2** either adopts a structure different from that seen in the crystal or else some fluxional process renders the methylene protons chemically equivalent on the ^{1}H NMR time scale. A static solution structure, possessing a plane of symmetry, or a fluxional process that involves "wing-flapping" of the bridging ligands can be rejected; each of these scenarios provides for the equivalency of the methylene protons but does not account for the anomalous ^{13}C NMR data of **2**.

Bridge–terminal exchange between two mutually trans carbonyl ligands is invoked to rationalize the spectroscopic observations of **2** and of the monophosphine complexes **3**. Figure 2 (IIa) shows a molecular plot of **2**, stripped of its η-C_5Me_5 and η-C_5H_5 ligands. From this viewpoint, it is clear that a bridging carbonyl ligand has a trans relationship with one of the terminal carbonyl groups. The other terminal carbonyl ligand is in a cis relationship to the μ-CO group, but is trans to the bridging methylene group. Rapid bridge–terminal exchange between the two (mutually trans) CO ligands that are cis to the μ-CH_2 group, along with a minimal net motion of the (η-C_5Me_5)Ni–W(η-C_5H_5) unit, should lend the molecule effective planar symmetry on the NMR time scale (Figure 2, IIa ⇌ IIb). The trans carbonyl ligands thus undergo pairwise exchange, but they always remain distinct from the unique carbonyl group that is trans to the μ-CH_2 group.

In addition to accounting for the equivalency of the C*H*$_2$ protons, this process explains the ^{13}C NMR spectrum of complex **2**. The fluxionality renders the two exchanging carbonyl groups equivalent on the ^{13}C NMR time scale. The chemical shift of the exchanging pair is intermediate to that of a terminal and that of a bridging carbonyl moiety. As such, this "averaged" signal is observed downfield from the resonance stemming from the unique, fully terminal carbonyl group. Two signals (in a 2:1 ratio) are seen for the carbonyl ligands as the exchanging pair never permutes with the unique CO group at low temperature.

At ambient temperatures the two carbonyl signals appear as broad resonances. It is possible that global carbonyl exchange is setting in at ambient or elevated temperature. Attempts to record a limiting ^{13}C NMR spectrum at higher temperature unfortunately resulted in the thermal decomposition of **2**.

The geometry of the phosphine complexes, as discussed earlier, is believed to incorporate one terminal and two bridging carbonyl ligands. In an analogous fashion, one of the bridging carbonyl groups is in a trans relationship to the terminal one. Rapid bridge–terminal exchange between these two ligands on the NMR time scale would lead to a single resonance in the ^{13}C NMR spectrum. Here, a unique carbonyl remains bridging and consequently its chemical shift resonance is displayed downfield from that of the exchanging ligands.

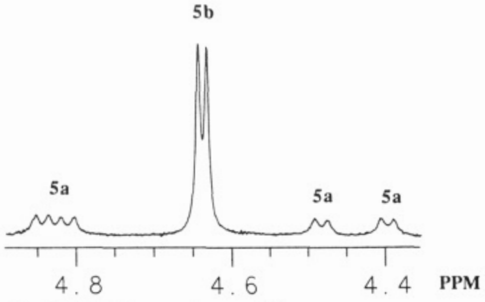
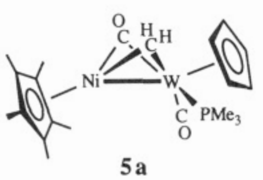


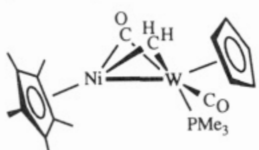
Figure 3. ^{1}H NMR spectrum of **5**.

The appearance of the ^{1}H NMR spectrum of **3b** supports the fluxional process being operative in this dimethylphenylphosphine complex. Methyl substituents on the dimethylphenylphosphine ligand appear as a single resonance (split by ^{31}P coupling to a doublet). Just as the effective mirror plane in complex **2** renders its methylene proton signals equivalent, the symmetry plane induced by the dynamic process accounts for the synchronous chemical shifts of the methyl groups in **3b**.

(c) Reaction of Complex 2 with PMe$_3$. As the two terminal ligands in **2** are in different environments, substitution of a single terminal CO group by another ligand may lead to geometrical isomers. In an attempt to isolate isomeric PMe_3 derivatives of **2**, 1 molar equiv of PMe_3 was stirred overnight with a hexanes solution of the methylene complex. Crystallization of the solution led to recovery of reddish-brown crystals. These were subsequently shown to be a mixture of the trans and cis isomers of the trimethylphosphine derivatives (η-C_5Me_5)Ni(μ-CO)(μ-CH_2)W(CO)(PMe_3)(η-C_5H_5) **5a** (cis) and **5b** (trans) that were present in a 5:4 ratio, respectively.



5a



5b

While the compounds were not separated from each other, and are probably in equilibrium,[13] the ^{1}H NMR spectra of each isomer could be unambiguously assigned. The C*H*$_2$ group proton signals for each isomer are key in elucidating the resonances of each isomer. Rapid bridge–terminal exchange of the carbonyl ligands in the trans isomer **5b** creates an effective mirror plane in the molecule on the ^{1}H NMR time scale. The C*H*$_2$ protons in this molecule (Figure 3) are thus isochronous and appear as a single resonance split by ^{31}P coupling.

In **5a**, even if bridge–terminal exchange is prevalent, this never results in the C*H*$_2$ nuclei becoming chemically equivalent. They are thus displayed as an AB spin system in the ^{1}H NMR spectrum of this compound (Figure 3). Each proton exhibits significant coupling to the ^{31}P nucleus (J_{PH} for the two protons are dissimilar).

The chlorophosphine PPh_2Cl appeared to react with **2**, but products from this reaction were poorly characterized and will not be discussed further. However, the reaction of **2** with the diarylphosphine ligand PPh_2H afforded better characterized species. The hexane-insoluble substitution products that were formed were subsequently shown to be a mixture of two compounds. The major

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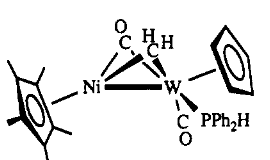
(13) This has not been established conclusively. However, different batches of **5** always contain a ~5:4 ratio of **5a**:**5b**.

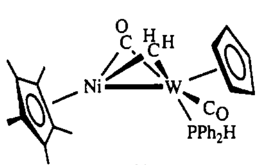
compound harvested was $(\eta\text{-}C_5Me_5)Ni(\mu\text{-}CO)(\mu\text{-}CH_2)W(CO)(PPh_2H)(\eta\text{-}C_5H_5)$ (**6a**, cis), accompanied by smaller quantities of its trans isomer $(\eta\text{-}C_5Me_5)Ni(\mu\text{-}CO)(\mu\text{-}CH_2)W(CO)(PPh_2H)(\eta\text{-}C_5H_5)$ (**6b**).

The isomers were not separated from each other. However, the same fluxional process functioning in **5** is active for complexes **6**, and NMR spectroscopy enabled unambiguous assignment of each compound's spectroscopic fingerprint. In a ^1H NMR spectrum of the mixture, both **6a** and **6b** exhibited signals for the PPh_2H proton. This signal appeared as a doublet with a characteristically large P–H coupling [$^1J_{PH}$ = 378 Hz (**6a**); $^1J_{PH}$ = 385 Hz (**6b**)] for each isomer. The ^1H NMR spectrum indicated that the CH_2 protons of the cis isomer **6a** are diastereotopic and are each split by a large P–H coupling and a smaller H–H coupling.[14] Resonances assigned to the CH_2 protons of the trans isomer are isochronous and are only split by a small ^{31}P coupling.

The fluxional process that creates an effective mirror plane in **6b** also renders the two phenyl groups in this species equivalent. The ^{13}C NMR spectrum validates this premise: resonances observed in the phenyl region of the spectrum can be assigned to two distinct phenyl rings for **6a**, and one set of signals can be assigned for the two mirror-related phenyl rings of **6b**. The cis isomer is more abundant than the trans isomer, in an even more skewed ratio than is found for **5a** and **5b** (5:4, respectively). Complexes **6a** and **6b** are in approximately a 5:1 ratio.



6a



6b

3. Reaction of Complex 1 with Potentially Bridging Species. (a) Addition of CO: Spectroscopic Properties of the Saturated Species $(\eta\text{-}C_5Me_5)Ni(\mu\text{-}CO)_2W(CO)_2(\eta\text{-}C_5H_5)$ (1a). In addition to trialkylphosphine groups, which invariably act as terminal ligands, and methylene groups, which usually bridge dimetal centers, a third set of ligands exists that can bind in a terminal and/or a bridging manner. Carbon monoxide is such a ligand, and as has been stated elsewhere,[8] the deep blue color of solutions of **1** rapidly gives way to a dark green hue when exposed to CO. IR analysis of the resultant solution shows that the saturated species $(\eta\text{-}C_5Me_5)Ni(\mu\text{-}CO)_2W(CO)_2(\eta\text{-}C_5H_5)$ (Ni–W) (**1a**) is regenerated. This process (eq 3) reverses the formation of **1**.

$$\underset{\mathbf{1a}}{(\eta\text{-}C_5Me_5)Ni(\mu\text{-}CO)_2W(CO)_2(\eta\text{-}C_5H_5)\ (Ni\text{-}W)} \rightleftharpoons \underset{\mathbf{1}}{(\eta\text{-}C_5Me_5)Ni\text{-}W(CO)_3(\eta\text{-}C_5H_5)\ (Ni\text{-}W)} + CO\uparrow \quad (3)$$

The ^{13}C NMR spectrum of **1a** at ambient temperatures exhibits a single carbonyl signal. The analogous (and more soluble) methylcyclopentadienyl species $(\eta\text{-}C_5Me_5)Ni(\mu\text{-}CO)_2W(CO)_2(\eta\text{-}C_5H_4Me)$ (Ni–W)[15] also exhibits a single resonance for all carbonyl groups at ambient and low temperatures (–60 °C). The observation of $^{183}W\text{–}^{13}C$ coupling invalidates CO ligand dissociation as a viable option. The observation of a single carbonyl resonance, even at low temperature, suggests that a low-energy fluxional process is operative. The magnitude of the $^{183}W\text{–}^{13}C$ coupling constant (117 Hz) is small and makes it likely that the four ligands are undergoing site exchange via bridge–terminal CO interconversions (consistent with the low activation barrier to the dynamic process). On a time-averaged basis, the $^{183}W\text{–}^{13}C$ coupling constant will be $\sim^3/_4$ that of a typical tungsten-bound carbonyl ligand coupling, as is observed. A low-energy $\nu(CO)$ stretch at $\sim$1795 cm^{-1} corroborates the presence of a μ-CO group.

(b) Reaction of 1 with ^tBuNC. Isocyanides (RNC:) are isoelectronic with CO and, like CO, are known to bond in either a terminal or a bridging fashion. Having elucidated the structural and spectroscopic features of both the trialkylphosphine and the methylene complexes of **1**, it was of interest to investigate whether similar isocyanide adducts were accessible.

Tetrahydrofuran solutions of **1** readily reacted with 1 equiv of ^tBuNC: an immediate color change was noted (blue to yellowish brown) on addition of the ligand at –78 °C. A tan product (**7**) was isolated from this reaction. Spectroscopic data (Tables I and II) suggested that this species was indeed an isocyanide adduct. Its ^1H NMR spectrum featured a broad singlet at δ 1.43 ppm (^tBu, 9 H) as well as peaks for $\eta\text{-}C_5Me_5$ and $\eta\text{-}C_5H_5$ proton resonances. The signal integration was in accord with a 1:1:1 ratio for the ^tBuNC, $\eta\text{-}C_5Me_5$, and $\eta\text{-}C_5H_5$ groups. A molecular formula consistent with these data is $(\eta\text{-}C_5Me_5)Ni(\mu\text{-}CO)(\mu\text{-}^tBuNC)W(CO)_2(\eta\text{-}C_5H_5)$ (Ni–W). The MS molecular ion peak of **7** tallied with this formulation. The formation of **7** is shown in eq 4.

$$\underset{\mathbf{1}}{(\eta\text{-}C_5Me_5)Ni\text{-}W(CO)_3(\eta\text{-}C_5H_5)} + {}^tBuNC \rightarrow \underset{\mathbf{7}}{(\eta\text{-}C_5Me_5)Ni(\mu\text{-}CO)(\mu\text{-}^tBuNC)W(CO)_2(\eta\text{-}C_5H_5)\ (Ni\text{-}W)} \quad (4)$$

IR data for this species are complex. Two terminal $\nu(NC)$ stretches at 2165 and 2136 cm^{-1} and a broad band in the μ_2-RNC region are observed. Four $\nu(CO)$ bands, two in the terminal and two in the bridging regions of the spectrum, were also visible. The IR spectrum indicates that **7** consists of interconverting isomers that are separately perceived on the IR time scale. Nevertheless, the dynamic process is too quick to be viewed on the slower ^1H NMR time scale and an averaged spectrum is recorded for the dynamic process. ^{13}C NMR data on the related (and more soluble) species $(\eta\text{-}C_5Me_5)Ni(\mu\text{-}CO)(\mu\text{-}^tBuNC)W(CO)_2(\eta\text{-}C_5H_4Me)$ corroborate the fluxionality of **7**. At –70 °C, two carbonyl resonances in a 2:1 ratio are observed in the ^{13}C NMR spectrum of this molecule. As the sample is warmed, the signals coalesce; at room temperature a single resonance is seen. This contrasts with the situation prevalent in **1a**, where the fluxional process cannot be arrested, even at low temperature. The nondegenerate intermediates/transition states involving terminal or bridging ^tBuNC groups lead to a higher activation energy for **7**.

Two independent fluxional processes are necessary to rationalize the observed data. For a closed structure (two μ_2-ligands), bridge–terminal exchange between mutually trans carbonyl ligands, and between the remaining carbonyl and isocyanide ligand, must be invoked. However, as only mutually trans groups (CO–CO or CO–^tBuNC) would exchange, such a process alone would not account for the single carbonyl ligand resonance noted at ambient temperatures in the ^{13}C NMR of **7**. To account for the degeneracy of all three carbonyl ligands, this dynamic

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[14] The magnitudes of these couplings and the chemical shifts of these signals are similar to the comparable CH_2 protons in the cis complex $(\eta\text{-}C_5Me_5)Ni(\mu\text{-}CO)(\mu\text{-}CH_2)W(CO)(PMe_3)(\eta\text{-}C_5H_5)$ (**5a**).

[15] IR evidence suggests that both complexes adopt structures that contain two μ_2-CO ligands. This constrasts with the nickel–cyclopentadienyl complex $(\eta\text{-}C_5H_5)(OC)Ni\text{-}W(CO)_3(\eta\text{-}C_5H_4Me)$ in which two of the tungsten-bound carbonyl ligands are, at most, semibridging to the nickel atom.

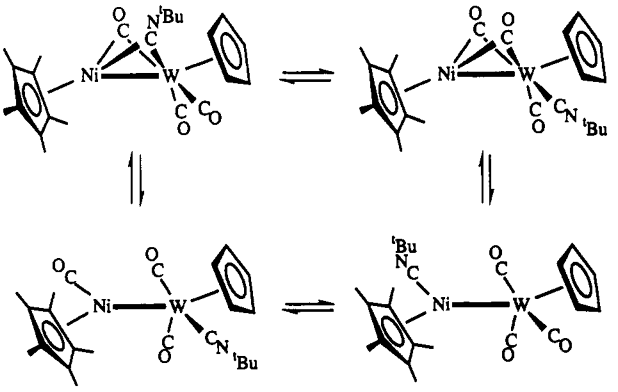


Figure 4. Possible interconverting isomers of **7**.

behavior must be coupled with rotation about the Ni–W bond. Allowing the closed structure to undergo bridge opening would facilitate metal–metal bond rotation. Bridge–terminal exchange at this stage would then result in the eventual permutation of all the carbonyl ligands. The multitude of IR ν(NC) bands, both terminal and bridging, can better be rationalized with the existence of both bridging and terminal ᵗBuNC isomers coexisting in solution.

The spectroscopic data for **7** are useful in determining the fluxional processes the molecule undergoes, but the actual structure adopted is more ambiguous. The two carbonyl ligand resonances noted in the ^{13}C NMR at −70 °C are in accord with one fluxional process (metal–metal bond rotation) being arrested while the other remains operative. The chemical shifts of the two signals differ by only ~4 ppm and are in a region of the spectrum that is intermediate between bridging and terminally bound CO groups. Possible interconverting isomers of **7** present in solution are depicted in Figure 4. (The syntheses of related (η-C_5H_5)Ni complexes are presented later in this paper.) It is noteworthy that isomers containing either terminal or bridging isocyanide ligands have been proposed to coexist in solutions of both $Ni_2(\eta$-$C_5H_5)_2(RNC)_2$ species and in $Mo_2(CO)_5(RNC)(\eta$-$C_5H_5)_2$ complexes.[16]

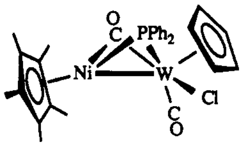
(c) Reaction of PPh$_2$Cl with Complex 1. (i) Formation of an Initial PPh$_2$Cl Adduct. The chlorophosphine species PPh$_2$Cl, and its analogue PPh$_2$H, may act as 2-electron donor ligands. However, the possibility of oxidative addition of the ligand exists here and may provide an entry into μ-phosphido species.

Complex **1** reacts at low temperature with PPh$_2$Cl to form an orange-brown adduct virtually quantitatively. This species has been isolated as an orange solid: the data indicate that this complex can be formulated as the chlorodiphenylphosphine species (η-C_5Me_5)Ni(μ-CO)$_2$W(CO)(PPh$_2$Cl)(η-C_5H_5) (**3d**). The structure of this compound is probably analogous to those of **3a**, **3b**, and **3c**. Its ^{31}P NMR spectrum shows a single resonance, flanked by ^{183}W satellites, whose magnitude (145 Hz) suggests a direct W–P bond. ^{1}H NMR data are in accord with this formulation.

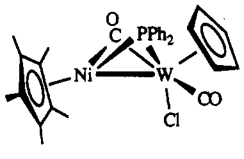
(ii) Oxidative Addition of the Ligand. When **3d** is maintained in solution and warmed to ambient temperatures, it slowly and irreversibly mutates to a reddish-brown mixture. A crop of brown-black crystals can be isolated from this final solution. Their NMR spectra show no signals that can be attributed to **3d**.

The ^{1}H and ^{13}C NMR spectra of these crystals suggest that they consist of two isomers in a ~2:1 ratio. Both species exhibit resonances arising from η-C_5H_5, η-C_5*Me*$_5$, and P*Ph*$_2$ groups. ^{1}H NMR signals for the η-C_5*H*$_5$ and η-C_5*Me*$_5$ groups (in each compound) are coupled to the ^{31}P nucleus and are split into doublets. The aromatic region of the ^{13}C NMR spectrum indicates that the two phenyl groups are related by a mirror plane in the mixture's major component. Two sets of signals are seen for the two phenyl groups of the minor isomer.

IR spectra also show two sets of two ν(CO) bands of very similar energy. These sets are observed in the terminal and bridging regions of the IR spectrum and are consistent with a terminal and a μ_2-CO group being present in each of the two compounds. The ^{31}P NMR data corroborate this: two signals, each spin coupled to ^{183}W, are noted in a ~2:1 ratio. In addition, the observation of ^{31}P coupling for the η-C_5H_5 and η-C_5*Me*$_5$ protons in both species suggests that, in each case, a PPh$_2$ ligand bridges the two metals. These results, coupled with microanalytical data, implied that these crystals were a mixture of cis and trans isomers of the oxidative addition product (η-C_5Me_5)Ni(μ-CO)(μ-PPh$_2$)W(CO)Cl(η-C_5H_5) (**8a**, cis isomer; **8b**, trans isomer) as shown.[17] As is observed in the PMe$_3$ complex **5b**, an effective mirror plane bisects the trans isomer, rendering the P*Ph*$_2$ groups equivalent on the NMR time scale.



8a, *cis* isomer



8b, *trans* isomer

A sample of the initial adduct **3d** was dissolved in acetone-d_6 at −20 °C, and its transformation into the mixture was monitored by VT ^{31}P NMR spectroscopy. Initially, traces of the cis isomer **8a** were observed in the spectrum, but virtually all the sample consisted of **3d**. As the sample was warmed to +10 °C, the resonance of the cis isomer grew in rapidly while that of **3d** decreased. Over a period of a few hours, the peak assigned to **3d** vanished; that of **8a** increased and then waned as **8b** slowly grew in.

(iii) Dynamic Equilibrium of Complexes 8a and 8b. Complexes **8a** and **8b** are in dynamic equilibrium with each other. This can be demonstrated by the reversible temperature-dependent changes seen in their relative ratio. A mixture of the isomers was dissolved in benzene-d_6 in a ^{1}H NMR tube and warmed to 60 °C. The spectrum revealed that the two isomers were in a ~1:1.7 ratio (**8a**:**8b**). As the temperature was lowered to 40 °C and then to 20 °C, the ratio increased to ~1:2, respectively: the two isomers reattained their higher temperature equilibrium relative ratio when the sample was warmed to 60 °C again. While these results are close to the boundaries of experimental integration errors, they are reproducible and are believed to reflect real changes.

The reaction pathway of **1** with PPh$_2$Cl can be rationalized in light of these data. Initially, an adduct is obtained in which the phosphine group binds (via the tungsten atom) to the unsaturated complex, affording **3d**. The ligand then undergoes oxidative addition across the dimetal center, expelling a carbonyl ligand as the PPh$_2$ group

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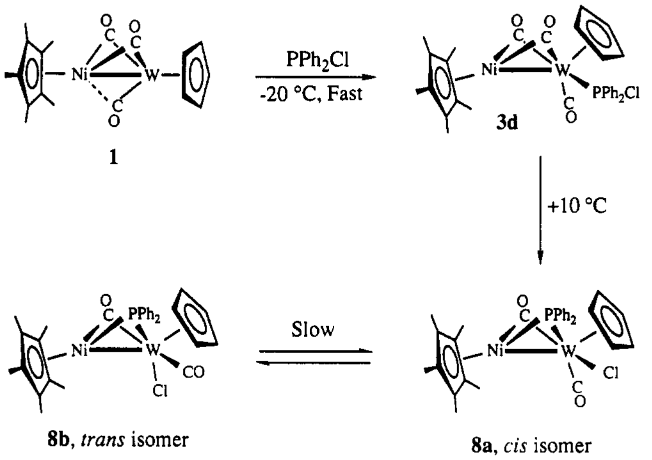
[16] Ni complexes: (a) Joshi, K. K.; Mills, O. S.; Pauson, P. L.; Shaw, B. W.; Stubbs, W. H. *Chem. Commun.* **1965**, 181. (b) Yamamoto, Y.; Hagihara, N. *Bull. Chem. Soc. Jap.* **1966**, *39*, 1084. Mo complexes: (c) Adams, R. D.; Brice, M.; Cotton, F. A. *J. Am. Chem. Soc.* **1973**, *95*, 6594.

[17] Alkylation of the mixture with MeLi affords a species whose MS spectrum has a parent ion at m/e = 699. This is consistent with substitution of a Cl group in **8a**/**8b** with a methyl group. Deck, K. J., unpublished results.

Scheme I



spans the Ni–W bond and the Cl binds in a terminal fashion to the tungsten atom. The kinetic oxidative addition product is, as expected,[18] the cis isomer **8a**. This product then isomerizes over a period of a few hours to give a thermodynamic mixture of the cis and trans isomers. These transformations are summarized in Scheme I.

The cis isomer is somewhat less soluble than the trans isomer, and crystallized samples of **8** tend to be fortified in **8a** relative to **8b**. However, neither isomer was isolated pure. An enrichment ratio of ~4.4:1 (**8a**:**8b**, by ^{1}H NMR spectroscopy) was the highest ratio realized. A chloroform-d_1 solution of this sample approached equilibrium slowly in solution: after ~3 h (monitored by ^{1}H NMR spectroscopy) the isomers were present in a 2.3:1 (**8a**:**8b**) ratio.

(d) Reaction of PPh_2H with Complex 1 and with a Ni–Mo Analogue. A dichloromethane solution of **1** reacts with PPh_2H at low temperature to yield an orange adduct. This species was isolated by hexane precipitation at low temperature. Spectral data on cold solutions suggest that it can be formulated as $(\eta\text{-}C_5Me_5)Ni(\mu\text{-}CO)_2W(CO)(PPh_2H)(\eta\text{-}C_5H_5)$ (**3e**). [The reaction was also performed on a Ni–Mo analogue of **1**, the complex $(\eta\text{-}C_5Me_5)Ni\text{–}Mo(CO)_3(\eta\text{-}C_5H_4Me)$.[7] The species $(\eta\text{-}C_5Me_5)Ni(\mu\text{-}CO)_2Mo(CO)(PPh_2H)(\eta\text{-}C_5H_4Me)$ (**3e′**) was recovered at -50 °C.]

As the temperature was raised, **3e** transformed to a green mixture. These *may* be the cis and trans isomers of the hydride phosphido complex $NiW(CO)_2(\mu\text{-}PPh_2)H(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)$ (**9**) that could result from the oxidative addition of PPh_2H to **1**. Resonances in ^{1}H and ^{31}P NMR data are consistent with this formulation, but the reaction is not clean and other species are present. [A weak hydride resonance observed in the ^{1}H NMR spectrum of the green solution is suspiciously close to that reported for $HW(CO)_3(\eta\text{-}C_5H_5)$ and is attributed to contamination by traces of this species.] In contrast to the related PPh_2Cl reaction, isomers **9** could not be isolated: their identity remains speculative. As the bright green solution was warmed, its color evolved to reddish brown and a ^{31}P NMR spectrum in dichloromethane showed that a new mixture of products was now present. Crystals isolated from this solution were shown to be isomers **8**, possibly resulting from chlorinated solvent attack on **9**.

To circumvent chlorination of any hydride species formed, the reaction of **1** with PPh_2H was repeated in toluene. At low temperature, the adduct **3e** appeared to be formed (by IR). When the solution was warmed to ambient temperatures, a different pathway was followed. The only isolated product was the salt containing the nickel cation $[Ni(PPh_2H)_2(\eta\text{-}C_5Me_5)]^+$ (**4e**$^+$) with $[W(CO)_3(\eta\text{-}C_5H_5)]^-$ as the counterion. This salt's tendency to oil and eventually separate from the toluene may govern the outcome of this reaction.

As **9** could not be isolated by following the above procedures, a different strategy was attempted. The complex $[Ni(PPh_2H)I(\eta\text{-}C_5Me_5)]$ was prepared in situ by the addition of I_2 and PPh_2H to $[Ni(\mu\text{-}CO)(\eta\text{-}C_5Me_5)]_2$ (Ni–Ni). This suspension was then treated with a solution of $[W(CO)_3(\eta\text{-}C_5H_5)]^-$. However, the tungsten anion did not appear to afford **3e** (based on IR data of a hexane extract). In a separate experiment, addition of excess diphenylphosphine to a cold 1:1 molar ratio of $[Ni(\mu\text{-}CO)(\eta\text{-}C_5Me_5)]_2$ and I_2 led to isolation of **4e**$^+$I$^-$, contaminated with a smaller quantity of $[Ni(PPh_2H)I(\eta\text{-}C_5Me_5)]$. [The latter complex was never isolated free of $[Ni(PPh_2H)_2(\eta\text{-}C_5Me_5)]^+I^-$, but its ^{1}H and ^{13}C NMR spectra were extracted from the mixture.]

4. Reactions of Saturated Nickel–Tungsten and Nickel–Molybdenum Complexes with PMe_3. (a) Reactions of $(\eta\text{-}C_5Me_5)Ni\text{–}W$ Species. In order to contrast the behavior of **1** with its saturated analogue, the reaction of complex **1a** with PMe_3 was studied. In an NMR tube experiment, the product of this reaction (in ≥95% yield) was **3a**, in which the phosphorus ligand is ligated to the *tungsten* atom. This substitution reaction thus affords the same reaction product as the additive reaction of **1** with this ligand.

An attempt was made to synthesize the nickel-bound isomeric species $(\eta\text{-}C_5Me_5)(PMe_3)Ni\text{–}W(CO)_3(\eta\text{-}C_5H_5)$ by using a procedure that mimicked the formation of **1a**. The nickel(II) trimethylphosphine complex $Ni(PMe_3)I(\eta\text{-}C_5Me_5)$[19] was prepared and treated with $[W(CO)_3(\eta\text{-}C_5H_5)]^-$. A reaction ensued, but the nickel-bound trimethylphosphine isomer was not realized: only $(\eta\text{-}C_5Me_5)Ni(\mu\text{-}CO)_2W(CO)(PMe_3)(\eta\text{-}C_5H_5)$ (**3a**) was isolated (eq 5), in a rarely observed example of a phosphine ligand

$$Ni(CO)I(\eta\text{-}C_5Me_5) + PMe_3 \rightarrow Ni(PMe_3)I(\eta\text{-}C_5Me_5) + CO\uparrow$$

$$Ni(PMe_3)I(\eta\text{-}C_5Me_5) + [W(CO)_3(\eta\text{-}C_5H_5)]^- \rightarrow \underset{\mathbf{3a}}{(\eta\text{-}C_5Me_5)Ni(\mu\text{-}CO)_2W(CO)(PMe_3)(\eta\text{-}C_5H_5)\ (Ni\text{–}W)} + I^- \quad (5)$$

migration reaction.[20] **3a** is likely obtained via transient formation of $(\eta\text{-}C_5Me_5)(PMe_3)Ni\text{–}W(CO)_3(\eta\text{-}C_5H_5)$, followed by dissociation of PMe_3 to form **1** and subsequent reassociation of **1** and PMe_3 to **3a**.

The selectivity by which phosphine and phosphite ligands bind to tungsten atoms upon reacting with either the saturated complex **1a** or the coordinatively unsaturated species **1** is noteworthy. Metal isomers are possible in principle, but only the tungsten-bound trimethylphosphine complexes are isolated here.

(b) Reactions of $(\eta\text{-}C_5H_5)Ni\text{–}M$ Species (M = Mo, W). The compound $(\eta\text{-}C_5H_5)(OC)Ni\text{–}W(CO)_3(\eta\text{-}C_5H_4Me)$ (**1b**) displays a solvent-dependent chemistry toward PMe_3. When **1b** is reacted with this ligand in ether, it undergoes

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(18) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. In *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 5, pp 279–343.

(19) While this species was not fully characterized, its cyclopentadienyl analogue $Ni(PMe_3)I(\eta\text{-}C_5H_5)$ has been.[19a] Related $(\eta\text{-}C_5Me_5)$ species are also known.[19b] (a) Mathey, F. *J. Organomet. Chem.* **1975**, *87*, 371. (b) Mise, T.; Yamazaki, H. *J. Organomet. Chem.* **1979**, *164*, 391.

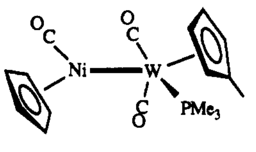
(20) The reaction of $Ni(PR_3)X(\eta\text{-}C_5H_5)$ with $Co(CO)_4^-$ results in a trialkylphosphine migration to afford $(\eta\text{-}C_5H_5)(CO)Ni\text{–}Co(CO)_3(PR_3)$: Manning, A. R. *J. Organomet. Chem.* **1972**, *40*, C73.

metal–metal bond cleavage and generates a salt as the only product. Two equivalents of PMe_3 are required per mole of **1b**: a deficiency of phosphine leads to the recovery of unreacted **1b**. The sparingly soluble salt contains the cationic Ni(II) species $[Ni(PMe_3)_2(\eta\text{-}C_5H_5)]^+$ (**4a**$^+$), with $[W(CO)_3(\eta\text{-}C_5H_5)]^-$ as the counterion. It was characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy. The ^1H NMR spectrum shows a characteristic virtual triplet pattern for the symmetry-related P*Me*$_3$ protons. No ^{183}W coupling is noted in the salt's ^{31}P NMR spectrum.

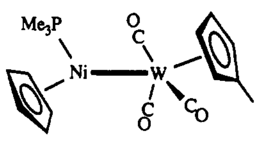
A hexane/ether solution of **1b** also afforded ionic species when reacted with dimethylphenylphosphine. The cation $[Ni(PMe_2Ph)_2(\eta\text{-}C_5H_5)]^+$ (**4b**$^+$) was spectroscopically identified. The related $[Ni(PMe_2Ph)_2(\eta\text{-}C_5Me_5)]^+$ cation is believed to be a decomposition product of $(\eta\text{-}C_5Me_5)Ni(\mu\text{-}CO)_2W(CO)(PMe_2Ph)(\eta\text{-}C_5H_5)$ (**3b**).

The reaction of **1b** with PMe_3 appeared to be solvent dependent. When these two species were combined in dichloromethane [in which the salt **4a**$^+[W(CO)_3(\eta\text{-}C_5H_4Me)]^-$ is soluble], the reaction proceeded differently. While the cation **4a**$^+$ is also present in the crude reaction mixture, none of this species was present in ^1H spectra of the worked up products. ^1H and ^{13}C NMR data are consistent with the products being a mixture of two isomers of empirical formula $NiW(CO)_3(PMe_3)(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Me)$ (**10a, 10b**). These isomers were inseparable in our hands but C/H microanalysis of the mixture corroborated their formulation as such. Both compounds exhibit singlets for the η-C$_5$*H*$_5$ and η-C$_5$H$_4$*Me* nuclei and doublets for the P*Me*$_3$ protons in ^1H and ^{13}C NMR spectra. Aromatic η-C$_5$*H*$_4$Me signals of both isomers indicate that an effective plane of symmetry bisects each $\eta\text{-}C_5H_4Me$ ring on the ^1H and ^{13}C NMR time scales.

We initially speculated that these species were isomers of the *tungsten*-bound trimethylphosphine compound $(\eta\text{-}C_5H_5)(CO)Ni\text{-}W(CO)_2(PMe_3)(\eta\text{-}C_5H_4Me)$, but the ^{31}P NMR spectrum invalidated this hypothesis. The mixture of **10a** and **10b** exhibits two singlets in the ^{31}P NMR spectrum. However, the chemical shifts of the two isomers are very different (δ −39.9 ppm for the major isomer **10a** and δ +6.7 ppm for **10b**). Furthermore, *only **10a*** exhibits coupling to tungsten-183 (J_{WC} = 211 Hz). The magnitude of this coupling and the chemical shift of this signal are both close to values observed for **3a** and indicate that there is a direct W–PMe_3 bond in **10a**. Tungsten–phosphorus coupling is lacking in **10b**: its chemical shift is similar to those found for cationic $[Ni(\eta\text{-}C_5R_5)P_2]^+$ species (Table IV). Complex **10b** should thus be formulated as the nickel-bound trimethylphosphine complex $(\eta\text{-}C_5H_5)(PMe_3)Ni\text{-}W(CO)_3(\eta\text{-}C_5H_4Me)$, while **10a** contains a tungsten-bound PMe_3 group and is analogous to **3a**. Unlike its C_5Me_5 analogue, the less electron rich nickel atom in **10b** is able to accommodate a trimethylphosphine ligand.



10a



10b

The relative proportions of **10a** and **10b** change with time. Initially, the ratios of **10a**:**10b**:**4a**$^+$ present in the crude reaction mixture are respectively 4:5:7. After purification, **4a**$^+$ is eliminated, and the **10a**:**10b** ratio is ~3:1. Over time, the relative quantity of **10a**, the tungsten-bound PMe_3 species appears to increase relative to **10b**, but the reason for this has not been determined. The isomers may slowly be approaching their equilibrium concentrations. Alternatively, **10a** may be the thermodynamically stable isomer to which the mixture is reverting. The possibility that **10b** is decomposing faster than **10a** in solution has also not been ruled out.

Cyclopentadienyl–nickel analogues of the ^tBuNC complex **7** can be obtained. The species $(\eta\text{-}C_5H_5)Ni(\mu\text{-}CO)_2W(CO)(^tBuNC)(\eta\text{-}C_5H_4Me)$ (Ni–W) (**7a**) is formed when **1b** was treated with ^tBuNC. The terminal ν(NC) signal noted in the solid-state IR spectrum of this species, in conjunction with a terminal and two bridging ν(CO) resonances, implies the presence of 2 μ-CO groups in this species. However, the multitude of IR ν(CO) and ν(NC) absorptions observed in the hexanes spectrum of **7a** indicates that it exists as a mixture of isomers in solution. **7a** decomposes readily into what is believed to be the cationic species $[Ni(^tBuNC)_2(\eta\text{-}C_5H_4Me)]^+$ and other uncharacterized products; a satisfactory C/H analysis could not be obtained.[21]

The related Ni–Mo species $(\eta\text{-}C_5H_5)Ni(\mu\text{-}CO)(\mu\text{-}^tBuNC)Mo(CO)_2(\eta\text{-}C_5H_4Me)$ (Ni–Mo) (**7b**) was prepared starting from the Ni–Mo complex $(\eta\text{-}C_5H_5)(OC)Ni\text{-}Mo(CO)_3(\eta\text{-}C_5H_4Me)$. Spectroscopic data for **7b** resemble those of its Ni–W analogue, but **7b** is more resistant to decomposition.

Conclusions

The unsaturated complex 1 has proven to be a reactive substrate for addition of 2-electron donor ligands—reactions with 1 were initiated at −78 °C, and all proceeded rapidly at this temperature. Given the unsaturated nature of 1, this high reactivity is not too surprising, but it is noteworthy that not all the homobimetallic unsaturated complexes react cleanly with both terminal and bridging-type ligands. Only $Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2$ (Rh=Rh) yields bimetallic products when treated with either PMe_3 or CH_2N_2. Phosphine and phosphite ligands bind selectively to the tungsten atom when reacting with 1 to give a heterobimetallic product. (Pentamethylcyclopentadiene)nickel-bound trialkylphosphine species are only obtained in conjunction with metal–metal bond scission and Ni(II) cations. Mixed-metal NiW(CO)$_3$L(η-C$_5$*Me*$_5$)(η-C$_5$H$_5$) species are significantly more stable than their NiW(CO)$_3$L(η-C$_5$*H*$_5$)$_2$ analogues toward metal–metal bond cleavage and the formation of cationic Ni(II) species.

There appears to be a delicate balance between the stability of ligand-substituted Ni–W species and ionic products in which the Ni–W bond has been ruptured. The outcome of a particular experiment depends on the reaction conditions, the amount of ligand present, and whether $(\eta\text{-}C_5Me_5)Ni\text{-}WL_n$ or $(\eta\text{-}C_5H_5)Ni\text{-}WL_n$ species are involved. The dienyl ring dependence probably arises more from electronic rather than from steric effects between the $\eta\text{-}C_5H_5$ and $\eta\text{-}C_5Me_5$ ligands. Manifestations of product dependence on solvent and/or ligands have precedent, even in the chemistry of homonuclear metal carbonyl dimer species. Thus, reaction of $Mo_2(CO)_6(\eta\text{-}C_5H_5)_2$ with 2-electron donors may afford $Mo_2(CO)_5L(\eta\text{-}C_5H_5)_2$ species, $Mo_2(CO)_4L_2(\eta\text{-}C_5H_5)_2$ complexes, or salts formulated as $[Mo(CO)_2L_2(\eta\text{-}C_5H_5)]^+[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$, depending on the reaction conditions, even in some cases with the same ligand.[22] Lattice energy and/or solvation effects can tip the balance in favor of one outcome or another.

We believe that the Ni(I) atom in 1 is too electron rich to accommodate a nucleophilic PMe_3 ligand: for C_5Me_5

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(21) The species $[Ni(^tBuNC)_2(\eta\text{-}C_5H_5)]^+$ has been reported: Yamamoto, Y.; et al. *J. Organomet. Chem.* **1969**, *18*, 189.

(22) Davis, R.; Kane-Maguire, L. A. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds: Pergammon Press: Oxford, UK, 1982; Vol. III, p 1179, and cited references.

species, net addition thus takes place at the tungsten center. Carbonyl substitution also ensues at a tungsten-bound carbonyl ligand in these compounds. Nickel-bound trialkylphosphine complexes are thus only observed in the more electron deficient Ni(II)(C_5Me_5) cationic systems. However the less electron rich nickel atom in (η-C_5H_5)Ni complexes can bind to a PMe_3 ligand without rupturing the metal–metal bond.

Experimental Section

(a) General Remarks. All manipulations were carried out by using Schlenk or vacuum line techniques under a nitrogen atmosphere. Solvents were predried over 4-Å molecular sieves and were distilled over sodium (toluene), sodium benzophenone ketyl (diethyl ether and hexanes), or CaH_2 (dichloromethane). Reagent grade acetone was stored over 4-Å molecular sieves and deoxygenated by bubbling nitrogen through it immediately prior to use. Deuterated NMR solvents and ^tBuNC (Aldrich) were subjected to three freeze–pump–thaw cycles and stored under an atmosphere of nitrogen prior to use. Phenylacetylene was purchased from Aldrich and used as received. Syntheses of 1, 1a, 1b, and (η-C_5Me_5)Ni(μ-CO)$_2$W(CO)$_2$(η-C_5H_4Me) (Ni–W) have been described.[7,23]

NMR spectra were obtained on General Electric NT-300 or GN-300 spectrometers at 20 °C in chloroform-d_1 unless otherwise stated. Cr(acac)$_3$ (0.01–0.05 M) was added to ^{13}C NMR samples as a shiftless relaxation reagent. IR spectra were recorded on an IBM IR-32 FT instrument, using the solvent-subtract function for solution spectra, or on a Perkin-Elmer 1420 IR spectrometer. Elemental analyses were performed by M-H-W Labs, Phoenix, AZ. Mass spectra were obtained on a Finnegan-Matt instrument operating in the CI mode for low-resolution spectra, with isobutane as the ionization source. EI was used for HRMS with PFK as a standard. All parent ions show the appropriate isotopomer pattern. The reported complexes are moderately soluble in hexanes, except for 1, 3a, and 3b, which are sparingly soluble in this solvent. The nonionic species are soluble in dichloromethane, chloroform, and toluene. Some are sparingly soluble in ether.

(b) Synthetic Data. Preparation of (η-C_5Me_5)Ni(μ-CO)$_2$W(CO)(L)(η-C_5H_5) [3a, L = PMe_3; 3b, L = PMe_2Ph; 3c, L = P(OMe)$_3$]. The phosphine adducts of 1 were all prepared in an analogous fashion: the synthesis of **3a** is given as a typical example. 1 (~260 mg, 0.50 mmol) was dissolved in CH_2Cl_2 (15 mL) and cooled to −78 °C. PMe_3 (1.00 mL of a 1.0 M THF solution, 1 mmol) was added. An instant color change (blue to orange) was noted. The reaction mixture was then warmed to 0 °C, and hexane (10 mL) was added. Solvents were then removed under reduced pressure, affording brownish-orange crystals of **3a** in essentially quantitative yield (>95% by ^1H NMR). For **3b** and **3c**, the isolated solids were rinsed with hexanes (2 × 5 mL) to remove unreacted PMe_2Ph and P(OMe)$_3$, respectively. MS (*m/e*) for **3a**: 604 (M^+), 576 $(M - CO)^+$, 528 $(M - PMe_3)^+$. MS (*m/e*) for **3b**: 666 (M^+), 638 $(M - CO)^+$, 528 $(M - PMe_2Ph)^+$.

Synthesis of (η-C_5Me_5)Ni(μ-CH_2)(μ-CO)W(CO)$_2$(η-C_5H_5) (2). A pure sample of 1 (~520 mg, 1.0 mmol) was dissolved in THF (35 mL) and cooled to −78 °C. The addition of CH_2N_2 (5 mL of a ~0.3 M solution in ether, ~1.5 mmol) via a flame-polished pipet led to vigorous gas evolution and an instantaneous color change (blue to brown). After the reaction mixture was allowed to warm to 0 °C, the solvent and excess CH_2N_2 were removed under reduced pressure into a trap containing acetic acid (to destroy unreacted CH_2N_2). The crude product was extracted with warm hexane (leaving behind a white, insoluble uncharacterized solid, possibly polyethylene) and filtered. Concentrating the filtrate and cooling the solution to −20 °C led to the isolation of **2** as large black crystals (two crops, net yield 410 mg, ~76%). Complex **2**, unlike its Ni–Mo analogue, decomposes when chromatographic purification is attempted.

Synthesis of Cis and Trans Isomers of (η-C_5Me_5)Ni(μ-CH_2)(μ-CO)W(CO)(PMe_3)(η-C_5H_5) (5a and 5b). PMe_3 (0.30 mL of a 1.0 M solution, 0.30 mmol) was added to a solution of **2** (150 mg, 0.28 mmol in 30 mL of hexane). The mixture was stirred overnight, and then the solvent was removed under reduced pressure. The residue was then extracted with CH_2Cl_2 and filtered. After concentration of the filtrate, hexane (10 mL) was added to the solution. Crystallization at −20 °C gave reddish-brown crystals of **5a** and **5b** in a 5:4 ratio (60 mg, 36%). Analysis IR of the mother liquor showed that only traces of product remained in solution.

Synthesis of Cis and Trans Isomers of (η-C_5Me_5)Ni(μ-CH_2)(μ-CO)W(CO)(PPh_2H)(μ-C_5H_5) (Ni–W) (6a and 6b). A solution of **2** (153 mg, 0.283 mmol) in hexane (30 mL) was treated with neat PPh_2H (60 μL, 0.34 mmol) at −65 °C. The solution was warmed to −20 °C, maintained there for 7.5 h, allowed to warm to ambient temperature, and stirred overnight. The supernatant solution was then removed from the precipitate that had formed. The solid material was washed with hexane (2 × 5 mL), taken up in dichloromethane/hexane (1:1) and filtered. Removal of the solvents was followed by a final hexane rinse. The brown solid was then pumped dry. Yield of (η-C_5Me_5)Ni(μ-CH_2)(μ-CO)W(CO)(PPh_2H)(η-C_5H_5) (Ni–W) (**6a** and **6b**): 90 mg, 0.13 mmol (46%). **6a**:**6b** ≈ 4.4:1, by NMR.

Synthesis of (η-C_5Me_5)Ni(μ-^tBuNC)(μ-CO)W(CO)$_2$(η-C_5H_5) (7). A crystalline sample of 1 (520 mg, 1.0 mmol) was dissolved in CH_2Cl_2 (30 mL) and chilled to −78 °C. ^tBuNC (0.12 mL, 2.0 mmol) was added, and an immediate color change (blue to brown) was observed. After the reaction mixture was gradually warmed to room temperature, hexane (15 mL) was added. Solvents were then removed under reduced pressure until complete precipitation had occurred to give a colorless solution. The remaining solvent was removed by syringe, and the black solid was rinsed with hexane (2 × 5 mL) to afford black crystals of **7**, judged pure (>95%) by ^1H NMR. MS (*m/e*): 609 (M^+), 581 $(M - CO)^+$, 528 $(M - {}^tBuNC)^+$. Anal. Calcd for $C_{23}H_{29}NiWNO_3$: C, 45.28; H, 4.79. Found: C, 45.44; H, 4.86.

Reaction of 1 with PPh_2Cl. (i) Isolation of (η-C_5Me_5)Ni(μ-CO)$_2$W(CO)(PPh_2Cl)(η-C_5H_5) (3d). A CH_2Cl_2 solution (11 mL) of 1 (610 mg, 1.20 mmol) was treated with neat PPh_2Cl (0.30 mL, 1.7 mmol) at −78 °C. The now orange solution was concentrated: subsequent addition of hexanes deposited a solid (**3d**) that was rinsed with ether and dried in vacuo. Yield: 820 mg, 1.10 mmol (92%). Anal. Calcd for $C_{30}H_{30}NiWClPO_3$: C, 48.20; H, 4.05. Found: C, 48.46; H, 4.25.

(ii) Formation of Cis and Trans Isomers of (η-C_5Me_5)Ni(μ-CO)(μ-PPh_2)W(CO)Cl(η-C_5H_5) (Ni–W) (8a ⇌ 8b). A solution of **3d** (704 mg, 0.94 mmol in CH_2Cl_2 (25 mL) was refluxed for 90 min. The solvent was then removed, and the residue was extracted with several 10–25-mL portions of a warm toluene/CH_2Cl_2 (4:1) mixture and filtered through a Celite pad. Concentration and cooling of the filtrate repeatedly yielded brown-black crystals of a mixture of isomers **8a** and **8b**. Net yield: 206 mg, 0.29 mmol (31%). Anal. Calcd for $C_{29}H_{30}NiWClPO_2$: C, 48.41; H, 4.20. Found: C, 48.69; H, 4.37. MS (*m/e*): 691 $(M - CO)^+$.

Reaction of (η-C_5Me_5)Ni–Mo(CO)$_3$(η-C_5H_4Me) with PPh_2H. PPh_2H (50 μL, 0.29 mmol) was added to a chilled (−78 °C) solution of (η-C_5Me_5)Ni–Mo(CO)$_3$(η-C_5H_4Me)[7] (0.30 mmol) in dichloromethane (7 mL). A red-orange solution resulted. Some solvent was removed at −50 °C, and the now more concentrated solution deposited microcrystals of (η-C_5Me_5)Ni(μ-CO)$_2$Mo(CO)(PPh_2H)(η-C_5H_4Me) (**3e′**). The observation of [Ni(μ-CO)(η-C_5Me_5)]$_2$ in the mother liquor indicated that significant decomposition had ensued.

Reaction of (η-C_5Me_5)Ni–W(CO)$_3$(η-C_5H_5) (1) with PPh_2H. (i) Isolation of (η-C_5Me_5)Ni(μ-CO)$_2$W(CO)(PPh_2H)(η-C_5H_5) (3e). A CH_2Cl_2 solution of 1 (263 mg, 0.50 mmol) was chilled to −78 °C, and PPh_2H (0.50 mL of a 1.10 M solution, 0.55 mmol) was added. The blue color of 1 dissipated within seconds and the solution turned orange. The solution was concentrated below 0 °C, and hexane was added. This resulted in the precipitation of **3e**. The orange powder was rinsed with hexanes and dried in vacuo.

(ii) Reaction of 1 with PPh_2H in Dichloromethane. Formation of the Isomeric Chloro Complexes (η-C_5Me_5)Ni(μ-CO)(μ-PPh_2)W(CO)Cl(η-C_5H_5) (8). PPh_2H (67 μL, 0.38 mmol) was added to a solution of 1 (200 mg, 0.37 mmol) in CH_2Cl_2. The blue solution turned orange and then brown within seconds. The solution was heated to reflux, during which time it became

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(23) Chetcuti, M. J.; Eigenbrot, C.; Green, K. A. *Organometallics* 1987, *6*, 2298.

bright green. After being refluxed for 3 h, the now brown solution was cooled, filtered, and pumped down to dryness. The residue was dissolved in warm toluene and layered with hexanes. Black microcrystals of 8 deposited at −20 °C after 4 days. These crystals were collected and rinsed with a 1:1 toluene/hexanes mixture while the process was repeated for the filtrate. Net yield of harvested product: 39 mg, 0.054 mmol (15%).

(iii) Reaction in Toluene. Formation of [Ni(PPh_2H)$_2$(η-C_5Me_5)]$^+$[W(CO)$_3$(η-C_5H_5)]$^-$. A toluene solution (25 mL) of 1 (60 mg, 0.11 mmol) was chilled to −60 °C. Neat PPh_2H (30 μL, 0.17 mmol) was added. The solution turned orange-brown within seconds, and the mixture was warmed to ambient temperature. It was stirred for 5 h, and the slurry was then transferred by cannula to a fresh vessel. Concentration led to an oily residue, which was pumped on in vacuum for several hours. A ^1H NMR spectrum of an acetone-d_6 solution of this material revealed that it consisted of **4e**$^+$[W(CO)$_3$(η-C_5H_5)]$^-$.

Reactions of (η-C_5H_5)(CO)Ni–W(CO)$_3$(η-C_5H_4Me) (1b) with PMe_3. (i) Reaction in Dichloromethane. Synthesis of NiW(CO)$_3$(PMe_3)(η-C_5H_5)(η-C_5H_4Me) (10a, 10b). PMe_3 (0.3 mL of a 1.0 M THF solution, 0.30 mmol) was added to a green CH_2Cl_2 solution of **1b** (156 mg, 0.31 mmol). The solution turned orange-brown over 4 h. The solvent was removed in vacuo. The residue was extracted with warm toluene (40 °C), and the brown filtrate was concentrated and cooled to −20 °C. Brown cubes of NiW(CO)$_3$(PMe_3)(η-C_5H_5)(η-C_5H_4Me) (**10a**, **10b**) (~55 mg, 0.10 mmol) were harvested from two successive crystallizations. Anal. Calcd for $C_{17}H_{21}NiWO_3P$: C, 37.34; H, 3.87. Found: C, 37.28; H, 4.09.

(ii) Reaction in Diethyl Ether. Formation of [Ni(PMe_3)$_2$(η-C_5H_5)]$^+$[W(CO)$_3$(η-C_5H_4Me)]$^-$. One equivalent of PMe_3 (0.30 mL of a 1 M THF solution, 0.30 mmol) was added to a solution of **1b** (143 mg, 0.29 mmol) in ether (20 mL). An orange precipitate formed immediately. Addition of another 1 equiv of PMe_3 resulted in the formation of more precipitate and completely discharged the green color of the remaining solution. The supernatant liquid was discarded, and the precipitate was rinsed with 2 × 5 mL of ether and dissolved in CH_2Cl_2. Addition of ether afforded tan-colored microcrystals of [Ni(PMe_3)$_2$(η-C_5H_5)]$^+$[W(CO)$_3$(η-C_5H_4Me)]$^-$. A similar experiment on a smaller scale [**1b**; 50 mg, 0.10 mmol; 0.20 mL of 1 M PMe_3 in THF, 0.20 mmol] afforded 22 mg of **4a**$^+$[W(CO)$_3$(η-C_5H_4Me)]$^-$ (0.035 mmol, 35%). Anal. Calcd for **4a**$^+$[W(CO)$_3$(η-C_5H_4Me)]$^-$, $C_{20}H_{30}NiWO_3P_2$: C, 38.56; H, 4.85. Found: C, 38.74; H, 4.93.

Reaction of (η-C_5H_5)(CO)Ni–W(CO)$_3$(η-C_5H_4Me) (1b) with PMe_2Ph To Form [Ni(PMe_2Ph)$_2$(η-C_5H_5)]$^+$[W(CO)$_3$(η-C_5H_4Me)]$^-$. Dimethylphenylphosphine (0.11 mL of a 3.5 M hexane solution, 0.39 mmol) was added to a solution of **1b** (133 mg, 0.28 mmol) in ether (20 mL). An orange solid precipitated out of the green solution. The supernatant was then removed via a syringe; the residue was rinsed with ether and was then dissolved in CH_2Cl_2. Ether addition led to reprecipitation of **4b**$^+$[W(CO)$_3$(η-C_5H_4Me)]$^-$ as a dull tan powder.

Reaction between (η-C_5H_5)(CO)Ni–M(CO)$_3$(η-C_5H_4Me) and ^{t}BuNC (M = Mo, W). (η-C_5H_5)(CO)Ni–W(CO)$_3$(η-C_5H_4Me) (740 mg, 1.48 mmol) was dissolved in a hexanes/diethyl ether (~15 mL:~10 mL) mixture in a degassed Schlenk tube equipped with a magnetic stirrer bar. The solution was then cooled to −78 °C using a dry ice/acetone bath, and ^{t}BuNC (0.17 mL, 1.62 mmol) was syringed in under N_2 flow. The reaction mixture was stirred and gradually warmed to room temperature, during which time a greenish precipitate crashed out of the solution. The solution containing the precipitate was pumped dry and the resulting yellow–brown solid dissolved in a 1:1 hexanes/ether mixture and subjected to chromatography on silica gel using a hexanes/ether mixture (~95:5) as the initial eluent. This resulted in the separation of the mixture into three bands colored red, blue-green, and olive green in order of elution. The first two bands did not separate well from each other and were not characterized. The major olive green band was collected, concentrated, and placed in a freezer at −20 °C. Golden crystals of (η-C_5H_5)Ni(μ-CO)(μ-^{t}BuNC)W(CO)$_2$(η-C_5H_4Me) (Ni–W) (**7a**) deposited (240 mg, 0.43 mmol, 29%). Anal. Calcd for $C_{19}H_{21}NiWNO_3$: C, 41.20; H, 3.82. Found: C, 39.21; H, 3.98. (Decomposition products were always observed in the NMR data for **7a**; these presumably affected the microanalyses results.) Complex **7b** was prepared similarly and obtained in comparable yield. Anal. Calcd for $C_{19}H_{21}NiMoNO_3$: C, 48.97; H, 4.54. Found: C, 48.87; H, 4.66.

X-ray Structural Determination of (η-C_5Me_5)Ni(μ-CO)(μ-CH_2)W(CO)$_2$(η-C_5H_5) (2). An orange-brown crystal of **2** was mounted in random orientation on a glass capillary tube and placed on an Enraf-Nonius CAD 4 diffractometer at 20 ± 1 °C. Cell constants and an orientation matrix were obtained from least squares refinement of 25 reflections in the range $25 \leq \theta \leq 28°$. The lack of systematic absences and subsequent successful least squares refinement indicated that the space group was $P\bar{1}$.

Data were corrected for Lorentz and polarization effects; an empirical absorption correction was applied.[24] A total of 4202 unique reflections were collected, and the 3575 with $I > 3\sigma(I)$ were used in refinement. The structure was solved on a VAX computer using SDP/VAX software and the SHELX-86[25] solution package. Remaining atoms were located from succeeding Fourier maps and refined by full-matrix least squares refinement. Hydrogen atoms, located and added to the structure factor calculations, were not refined. Scattering factors were from Cromer and Waber.[26] Anomalous dispersion effects were included in F_c.[27,28] The highest peak in the final difference Fourier had a height of 3.48 e/Å^3 (estimated error based on $\Delta F = 0.19$). The weight w was defined according to the Killean and Lawrence method[29] with terms of 0.020 and 1.0; the function minimized was $\sum w(|F_o| - |F_c|)^2$. Plots of $\sum w(|F_o| - |F_c|)^2$ vs $|F_o|$, reflection order in data collection, sin θ/λ, and various classes of indices showed no unusual trends.

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Supplementary Material Available: Full tables of bond lengths, bond angles, positional parameters for hydrogen atoms, and thermal parameters for all atoms of complex 2 (7 pages). Ordering information is given on any current masthead page.

OM9106847

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