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Steric and “Indenyl” Effects in the Chemistry of Alkylidyne Complexes of Tungsten and Molybdenum

Stephen Anderson, Anthony F. Hill,* and Bashir A. Nasir

Department of Chemistry, Imperial College, London SW7 2AY, U.K.

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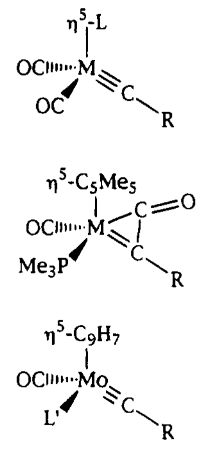
Reaction between LiC_5Me_5 or KC_9H_7 and $[M(\equiv C_6H_3Me_2\text{-}2,6)(CO)_2(NC_5H_4Me\text{-}4)_2Br]$ affords the complexes $[M(\equiv CC_6H_3Me_2\text{-}2,6)(CO)_2L]$ ($L = \eta\text{-}C_5Me_5$, M = W (**1a**); Mo (**1b**); $L = \eta^5\text{-}C_9H_7$, M = Mo (**1c**)). The complexes **1a** and **1b** react with PMe_3 to give η^2-ketenyl compounds $[M\{\eta^2\text{-}C(O)CC_6H_3Me_2\text{-}2,6\}(CO)(PMe_3)(\eta\text{-}C_5Me_5)]$ (M = W (**2a**), Mo (**2b**)) while the reaction of **1c** with PMe_3 or $P(OMe)_3$ gives $[Mo(\equiv CC_6H_3Me_2\text{-}2,6)(CO)L'(\eta^5\text{-}C_9H_7)]$ ($L' = PMe_3$ (**3a**), $P(OMe)_3$ (**3b**)). Thermolysis of **2a** provides **1a** rather than the anticipated complex $[W(\equiv CC_6H_3Me_2\text{-}2,6)(CO)(PMe_3)(\eta\text{-}C_5Me_5)]$. Compound **1b** has been employed to prepare the range of heterobimetallic compounds $[MoFe(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_5(\eta\text{-}C_5Me_5)]$ (**4**), $[MoFe(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_3(\mu\text{-dppm})(\eta\text{-}C_5Me_5)]$ (**5**), $[MoFe(\mu\text{-}\eta^2\text{-}SeCC_6H_3Me_2\text{-}2,6)(CO)_5(\eta\text{-}C_5Me_5)]$ (**6**), and $[MoCu(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)(\mu\text{-}CO)(\eta\text{-}C_5Me_5)_2]$ (**8b**), with bonds between molybdenum and iron or copper supported by the xylylmethylidyne unit, to assess the effects of steric encumbrance on bridge-assisted cluster asembly.

Introduction

The compounds $[M(\equiv CR)(CO)_2L]$ (M = Cr, Mo, W, Mn^+, Re^+; R = alkyl, aryl, alkynyl; $L = \eta\text{-}C_5H_5$, $\eta\text{-}C_5Me_5$, $HB(pyrazol\text{-}1\text{-}yl)_3$) have proven to be useful precursors for the synthesis of metal cluster compounds in which alkylidyne groups bridge metal–metal bonds.[1] In these studies, however, it has become increasingly obvious that considerations of steric bulk are of primary importance in dictating the geometries and degree of coordinative saturation in the resulting polymetallic species.[2] In particular, the reactions of the (alkylidyne)tungsten complex $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5Me_5)]$ were informative: with $[Fe_2(CO)_9]$ the major products are the bimetallic species $[WFe(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_n(\eta\text{-}C_5Me_5)]$ (n = 5, 6),[3] while similar treatment of $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ leads to the trinuclear derivatives $[WFe_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ and $[WFe_2\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_6(\eta\text{-}C_5H_5)]$.[4] Alternatively, the steric bulk may be increased by variation of the alkylidyne substituent, as shown by the reaction of $[W(\equiv CC_6H_3Me_2\text{-}2,6)(CO)_2(\eta\text{-}C_5H_5)]$ with $[Fe_2(CO)_9]$, which produces exclusively the dinuclear 32-valence-electron complex $[WFe(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_5(\eta\text{-}C_5H_5)]$[2a] with no indication of the formation of complexes of higher nuclearity or coordinative saturation.

We describe herein the synthesis and reactions of complexes $[M(\equiv CC_6H_3Me_2\text{-}2,6)(CO)_2L]$ ($L = \eta\text{-}C_5Me_5$, M = W (**1a**), Mo (**1b**); $L = \eta^5\text{-}C_9H_7$, M = Mo (**1c**)) which combine steric congestion at the metal center and alkylidyne substituent. The effect of this steric encumbrance is then assessed in reactions expected to be sensitive to such pressures. In ligand addition reactions of **1c** there is strong evidence for “indenyl” effects.

Chart 1. Alkylidyne and Ketenyl Complexes of Tungsten and Molybdenum[a]



1a M = W; L = C_5Me_5
1b M = Mo; L = C_5Me_5
1c M = Mo, L = C_9H_7

2a M = W
2b M = Mo

3a L' = PMe_3
3b L' = $P(OMe)_3$

[a] R = $C_6H_3Me_2$-2,6.

Results and Discussion

The γ-picoline-stabilized (alkylidyne)metal complexes $[M(\equiv CR)(CO)_2(NC_5H_4Me\text{-}4)_2Br]$ (R = $C_6H_3Me_2$-2,6) offer increased thermal stability over the tetracarbonyl derivatives $[M(\equiv CR)(CO)_4X]$, and this feature greatly enhances the convenience and yields involved in the introduction of the ligands $\eta\text{-}C_5H_5$, $\eta\text{-}C_5Me_5$, and $\eta^5\text{-}C_9H_7$. For our work we employed a modification of Mayr's method for the preparation of $[W(\equiv CPh)(CO)_2(py)_2(O_2CCF_3)]$[5] via the reaction of $[W(CO)_6]$ with PhLi, followed by cation metathesis to provide $[NMe_4][W\{C(=O)R\}(CO)_5]$, which is then reacted with $(CF_3CO)_2O$ and pyridine. We find that if the cation metathesis step is omitted, then the process may be conveniently carried out in one pot to provide $[W(\equiv CC_6H_3\text{-}$

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Table 1. Analytical[a] and Physical Data for the Complexes

			analyses (%)	
compd (R = $C_6H_3Me_2$-2,6)	yield (%)	IR $\nu_{max}(CO)^b/cm^{-1}$	C	H
$[W(\equiv CR)(CO)_2(\eta\text{-}C_5Me_5)]$ (**1a**, red)	67	1970 vs, 1892 vs	51.5 (51.2)	5.2 (4.9)
$[Mo(\equiv CR)(CO)_2(\eta\text{-}C_5Me_5)]$ (**1b**, red)	70	1979 vs, 1903 vs	62.4 (62.4)	6.4 (6.0)
$[Mo(\equiv CR)(CO)_2(\eta^5\text{-}C_9H_7)]$ (**1c**, red)	63	1998 vs, 1925 vs	62.4 (62.5)	4.3 (4.2)
$[W(\eta^2\text{-}OCCR)(CO)(PMe_3)(\eta\text{-}C_5Me_5)]$ (**2a**, violet)	84	1898 vs, 1729 m (br)	49.2 (50.7)	5.9 (5.5)
$[Mo(\eta^2\text{-}OCCR)(CO)(PMe_3)(\eta\text{-}C_5Me_5)]$ (**2b**, violet)	80	1888 vs, 1733 w (br)	60.2 (60.0)	7.2 (6.9)
$[Mo(\equiv CR)(CO)(PMe_3)(\eta^5\text{-}C_9H_7)]$ (**3a**)	62	1887 vs	60.3 (61.1)	6.1 (5.8)
$[Mo(\equiv CR)(CO)\{P(OMe)_3\}(\eta^5\text{-}C_9H_7)]$ (**3b**, yellow)	66	1910 vs	55.4 (55.0)	4.4 (5.3)
$[MoFe(\mu\text{-}CR)(CO)_5(\eta\text{-}C_5Me_5)]$ (**4**, violet)	61	2038 vs, 1975, 1965 s, 1859 w (br)	52.8 (53.0)	4.5 (4.4)
$[MoFe(\mu\text{-}CR)(CO)_3(\mu\text{-}dppm)(\eta\text{-}C_5Me_5)]$ (**5**, green)	89	1962 vs, 1907 s, 1748 w (br)	64.1 (64.7)	5.8 (5.3)
$[MoFe(\mu\text{-}\eta^2\text{-}SeCR)(CO)_5(\eta\text{-}C_5Me_5)]$ (**6**, orange)	83	2038 vs, 1976 s, 1962 m (sh), 1945 w (sh) 1903 w (br)	46.0 (46.3)	4.2 (3.9)
$[MoCu(\mu\text{-}CR)(CO)_2(\eta\text{-}C_5Me_5)_2]$ (**8b**, blue)	60	1950 vs, 1856 s	60.3 (61.7)	6.7 (6.5)
$[Mo(\kappa^2\text{-}S_2CR)(CO)_2(\eta\text{-}C_5Me_5)]$ (**9**, pink)	71	1952 vs, 1876 s	53.1 (53.8)	5.4 (5.2)

[a] Calculated values given in parentheses. [b] Data for dichloromethane solutions.

Me_2-2,6)$(CO)_2(NC_5H_4Me\text{-}4)_2Br]$. The presence of a bromide ligand in the final product was initially surprising; however, this originates from the 1 equiv of lithium bromide present as a consequence of the lithium reagent synthesis. The γ-picoline ligand was chosen purely for spectroscopic (^1H NMR) purposes.

Heating a solution of $[W(\equiv CC_6H_3Me_2\text{-}2,6)(CO)_2(NC_5H_4\text{-}Me\text{-}4)_2Br]$ and LiC_5Me_5 in tetrahydrofuran leads to clean formation of the pentamethylcyclopentadienyl complex $[W(\equiv CC_6H_3Me_2\text{-}2,6)(CO)_2(\eta\text{-}C_5Me_5)]$ (**1a**) in high yield. The molybdenum alkylidynes $[Mo(\equiv CC_6H_3\text{-}Me_2\text{-}2,6)(CO)_2(L)]$ (L = η-C_5Me_5 (**1b**), η^5-C_9H_7 (**1c**)) are obtained in a similar manner from $[Mo(\equiv CC_6H_3Me_2\text{-}2,6)(CO)_2(NC_5H_4Me\text{-}4)_2Br]$ and LiC_5Me_5 or KC_9H_7, respectively, with the exception that the reactions proceed readily at room temperature. Data for the complexes **1a**–**c** are given in Tables 1 and 2 and are unremarkable. Indenyl(alkylidyne)molybdenum complexes have been prepared previously by hydrogen-transfer reactions of suitable σ,π-vinyl precursors, a reaction clearly not applicable to the synthesis of arylmethylidyne complexes.[6]

The reactions of the complexes **1a**–**c** with trimethylphosphine were investigated in order to compare the results with those obtained previously and in view of the current interest in the formation of ketenyl complexes *via* alkylidyne–carbonyl coupling.[7,8] Typically, reaction of the compounds $[M(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ with phosphines leads to either simple substitution of a carbonyl ligand or formation of ketenyl ligands. In some cases the ketenyl complexes formed may be decarbonylated to give the phosphine-substituted product;[9] however, this is not generally the case.

Reaction of the compounds **1a** and **1b** with PMe_3 in tetrahydrofuran both lead to the η^2-ketenyl complexes $[M\{\eta^2\text{-}C(O)CC_6H_3Me_2\text{-}2,6\}(CO)(PMe_3)(\eta\text{-}C_5Me_5)]$ (M = W (**2a**), Mo (**2b**)), in contrast with the corresponding reaction of $[W(\equiv CC_6H_3Me_2\text{-}2,6)(CO)_2(\eta\text{-}C_5H_5)]$ (**1c**), in which a mixture of $[W(\equiv CC_6H_3Me_2\text{-}2,6)(CO)(PMe_3)(\eta\text{-}C_5H_5)]$ (**3c**) and $[W\{\eta^2\text{-}C(O)CC_6H_3Me_2\text{-}2,6\}(CO)(PMe_3)(\eta\text{-}C_5H_5)]$ (**2c**) is obtained. Excess phosphine fails to induce formation of a monodentate ketenyl complex, as has been observed in the reaction of $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ with excess PMe_3 to provide $[W\{C(CO)C_6H_4Me\text{-}4\}(CO)(PMe_3)_2(\eta\text{-}C_5H_5)]$.[10] Surprisingly, heating **2a** in tetrahydrofuran results in loss of PMe_3 rather than CO, as might have been expected with re-formation of the dicarbonyl precursor **1a**.

Substitution reactions at metal centers ligated by the η^5-indenyl ligand are often faster than for analogous η-C_5H_5 and η-C_5Me_5 derivatives, this being the so-called "indenyl effect" attributed to transient coordinatively unsaturated η^3-indenyl species.[11] The reaction of **1c** with PMe_3 was therefore of interest. Treating **1c** with PMe_3 leads to rapid formation of the phosphine-substituted alkylidyne complex $[Mo(\equiv CC_6H_3Me_2\text{-}2,6)(CO)(PMe_3)(\eta^5\text{-}C_9H_7)]$ (**3a**), with no evidence for the formation of ketenyl intermediates. Similarly, reaction of **1c** with trimethyl phosphite leads to $[Mo(\equiv CC_6H_3\text{-}Me_2\text{-}2,6)(CO)\{P(OMe)_3\}(\eta^5\text{-}C_9H_7)]$ (**3b**). The related complex $[Mo(\equiv CC_6H_4OMe\text{-}2)(CO)\{P(OMe)_3\}(\eta\text{-}C_5H_5)]$ (**3c**) may be prepared either by photolysis (12 h, low-power visible light) of $[Mo(\equiv CC_6H_4OMe\text{-}2)(CO)_2(\eta\text{-}C_5H_5)]$ in the presence of trimethyl phosphite or by reaction of

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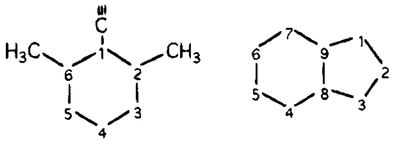
Table 2. Hydrogen-1 NMR Data[a] for the Complexes



compd	1H (δ)
1a ($CDCl_3$)	2.19 [s, 15 H, $C_5\mathit{Me}_5$], 2.46 [s, 6 H, $C_6H_3\mathit{Me}_2$], 6.87, 7.11 [m × 2, 3 H, $C_6\mathit{H}_3Me_2$]
1b (CD_2Cl_2)	2.06 [s, 15 H, $C_5\mathit{Me}_5$], 2.53 [s, 6 H, $C_6H_3\mathit{Me}_2$], 6.85, 6.99 [m × 2, 3 H, $C_6\mathit{H}_3Me_2$]
1c ($CDCl_3$)	2.48 [s, 6 H, $C_6H_3\mathit{Me}_2$], 5.89 [t, 1 H, $H^2(C_9H_7)$, *J*(HH) 3.1 Hz], 6.15 [d, 2 H, $H^{1,3}(C_9H_7)$, *J*(HH) 3.1 Hz], 6.86, 6.96, 7.42 [m × 3, 7 H, $C_6\mathit{H}_4$ and $C_6\mathit{H}_3$]
2a (CD_2Cl_2)	1.49 [d, 9 H, $P\mathit{Me}_3$, *J*(PH) 9.2 Hz], 1.85 [s, 3 H, $C_6H_3\mathit{Me}_2$], 1.93 [s, 15 H, $C_5\mathit{Me}_5$], 2.21 [s, 3 H, $C_6H_3\mathit{Me}_2$], 6.91, 7.02 [m × 2, 3 H, $C_6\mathit{H}_3$]
2b (CD_2Cl_2)	1.38 [d, 9 H, $P\mathit{Me}_3$, *J*(PH) 8.8 Hz], *ca* 1.78 [s(br), 3 H, $C_6H_3\mathit{Me}_2$], 1.82 [s, 15 H, $C_5\mathit{Me}_5$], 2.17 [s(br), 3 H, $C_6H_3\mathit{Me}_2$], 6.96, 7.00 [m × 2, 3 H, $C_6\mathit{H}_3$]
3a ($CDCl_3$)	1.18 [d, 9 H, $P\mathit{Me}_3$, *J*(PH) 8.4 Hz], 2.47 [s, 6 H, $C_6H_3\mathit{Me}_2$], 5.85 [d, 2 H, $H^{1,3}(C_9H_7)$, *J*(HH) 2.8 Hz], 6.23 [t, 1 H, $H^2(C_9H_7)$, *J*(HH) 3.11 Hz], 6.82, 6.8, 7.30 [m × 3, 7 H, $C_6\mathit{H}_4$ and $C_6\mathit{H}_3$]
3b (CDCl3)	2.51 [s, 6 H, $C_6H_3\mathit{Me}_2$], 3.22 [d, 9 H, $POC\mathit{H}_3$, *J*(PH) 14 Hz], 5.84 [t, 1 H, $H^2(C_9H_7)$, *J*(HH) 3.1 Hz], 5.98, 6.22 [m × 2, 2 H, 2 H, $H^{1,3}(C_9H_7)$], 6.82, 6.84, 6.91, 7.3−7.4 [m × 4, 7 H, $C_6\mathit{H}_4$ and $C_6\mathit{H}_3$]
4 ($CDCl_3$)	1.55 [s, 6 H, $C_6H_3\mathit{Me}_2$], 1.71 [s, 15 H, $C_5\mathit{Me}_5$], 7.04 [m, 3 H, $C_6\mathit{H}_3$]
5 ($CDCl_3$)	1.46 [s, 15 H, $C_5\mathit{Me}_5$], 1.83, 1.92 [s × 2, 6 H, $C_6H_3\mathit{Me}_2$], 4.48, 5.24 [m × 2, 2 H, $P_2C\mathit{H}_2$], 6.44, 6.69, 6.74, 7.00, 7.11, 7.36, 7.78 [m × 6, 23 H, $C_6\mathit{H}_5$ and $C_6\mathit{H}_3$]
6 ($CDCl_3$)	1.88 [s, 15 H, $C_5\mathit{Me}_5$], 2.47, 2.63 [s × 2, 6 H, $C_6H_3\mathit{Me}_2$], 7.13 [m, 3 H $C_6\mathit{H}_3$]
8b ($CDCl_3$)	1.67 [s, 30 H, $MoC_5\mathit{Me}_5$ and $CuC_5\mathit{Me}_5$], 1.99 [s, 6 H, $C_6H_3\mathit{Me}_2$], 7.00 [m, 3 H, $C_6\mathit{H}_3$]
9 (CD_2Cl_2)	1.95 [s, 15 H, $C_5\mathit{Me}_5$], 2.00, 2.27 [s × 2, 6 H, $C_6H_3\mathit{Me}_2$], 7.02, 7.12 [m × 2, 3 H, $C_6\mathit{H}_3$]

[a] Chemical shifts (δ) in ppm, coupling constants in Hz, measurements at room temperature.

$[Mo(\equiv CC_6H_4OMe\text{-}2)Cl(CO)\{P(OMe)_3\}_3]$ with sodium cyclopentadienide. The formation of the simple phosphite substitution complex **3c** by *photolysis* is itself somewhat unusual, since Geoffroy has shown that ketenyl complexes are usually the photoproducts in related systems.[9] These transformations are summarized in Scheme 1.

The reactions of complex **1b** with metal−ligand fragments were addressed next. As mentioned above, permethylation of the cyclopentadienyl ligand or the 2,6-positions of the arylmethylidyne ligand in the complex $[W(\equiv C\text{−aryl})(CO)_2(\eta\text{-}C_5H_5)]$ introduces considerable steric congestion into the tungsten coordination sphere.[2,3] This is manifest in the reactions of $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5Me_5)]$,[3] where treatment with coordinatively unsaturated metal−ligand fragment precursors lead in general to complexes of lower nuclearity than do those reactions involving the analogous cyclopentadienyl derivatives.

Reaction of **1b** with $[Fe_2(CO)_9]$ leads to exclusive formation of the 32-valence-electron bimetallic complex $[MoFe(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_5(\eta\text{-}C_5Me_5)]$ (**4a**). Most conspicuous among the spectroscopic data for such a complex[2] is the abnormally low field shift in the ^{13}C resonance due to the bridging carbyne carbon nucleus. This has been interpreted[3] by reference to similar downfield shifts observed in the ^{13}C NMR data for coordinatively unsaturated complexes of alkynes which have been extensively documented by Templeton and co-workers.[12] Such a low-field resonance is observed for **4a** at δ 404.2 ppm. The formal coordinative unsaturation of **4a** is reflected in its reactions with bis(diphenylphosphino)methane (dppm) and elemental selenium to provide respectively $[Fe(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_3(\mu\text{-}dppm)(\eta\text{-}C_5Me_5)]$ (**5**) and $[Fe(\mu\text{-}\eta^2\text{-}SeCC_6H_3Me_2\text{-}2,6)(CO)_5(\eta\text{-}C_5Me_5)]$ (**6**), which are analogous to derivatives of the simple cyclopentadienyl-ligated compounds.[2a,13,14]

A departure in the reactivity of **1b** from that of $[M(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$, which is clearly steric in origin, is observed in its reaction with the "$Cu(\eta\text{-}C_5Me_5)$" transfer reagent obtained from CuCl and LiC_5Me_5 in tetrahydrofuran.[15] This reagent (presumably $[Cu(thf)(\eta\text{-}C_5Me_5)]$) reacts with $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ to provide the trimetallic complex $[WCu_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)_2]$ (**7**), with no evidence being obtained for the presumed transient intermediate bimetallic complex $[WCu(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ (**8a**). Such a complex is, however, isolated in the reaction of **1b** with the transfer reagent. The deep blue species $[WCu(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_2(\eta\text{-}C_5H_5)(\eta\text{−}C_5Me_5)]$ (**8b**) is the only product isolated from this reaction even when the organocopper reagent is used in excess. The presence of a carbyne group bridging two metals is supported by the low-field shift of the carbyne carbon resonance (δ 319.2 ppm), which is considerably lower than that for **7** which is observed at δ 275.5 ppm. Infrared data for the carbonyl ligands (ν(CO) 1950, 1856 cm^{-1}) suggest that one of these adopts a semibridging role, partially alleviating the excessive electron density at the electron-rich d^{10} (formally) copper center. ^{13}C NMR data, however, indicate that the terminal and semibridging carbonyls interchange in solution (single resonance at δ 228.5 ppm).

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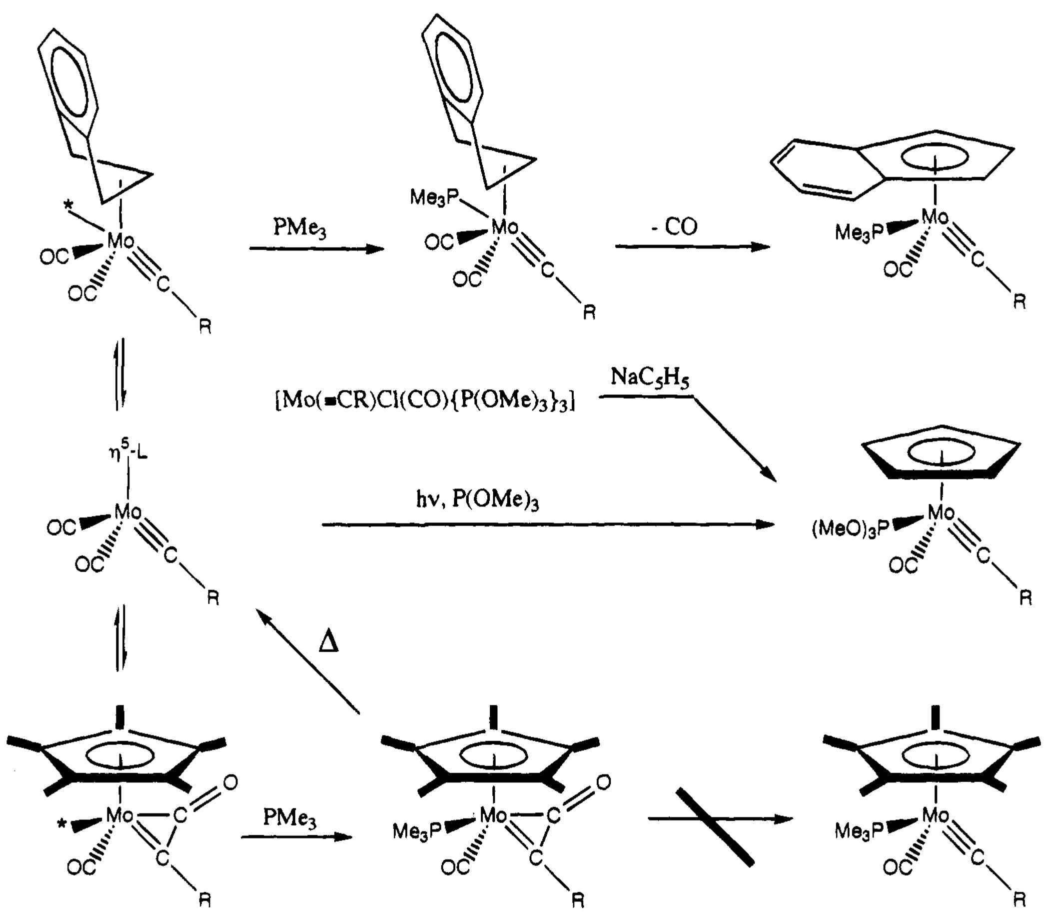
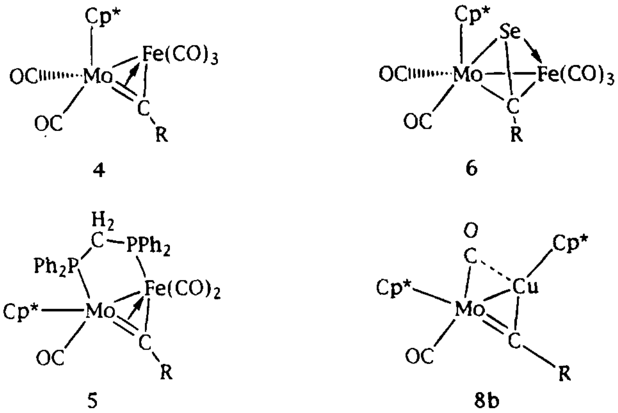
Scheme 1. Ligand Substitution via Ketenyl Formation or Indenyl Ring Slippage[a]



[a] L = C_5H_5, C_5Me_5, C_9H_7; * = vacant coordination site.

Chart 2. Alkylidyne-Bridged Bimetallic Complexes[a]



[a] R = $C_6H_3Me_2$-2,6; Cp* = η^5-C_5Me_5.

Two different types of ligands result from the reactions of terminal carbyne complexes with elemental sulfur. The electron-rich osmium carbyne [Os(≡CC_6H_4-Me-4)Cl(CO)(PPh_3)$_2$] reacts to provide the thiobenzoyl complex [Os(η^2-SCC_6H_4Me-4)Cl(CO)(PPh_3)$_2$],[16] which fails to react with further sulfur. In contrast, the half-sandwich carbyne complex [W(≡CC_6H_4Me-4)(CO)$_2$(η-C_5H_5)] reacts with either sulfur or selenium to provide the dithio- or diselenobenzoate complexes [W(κ^2-A_2-CC_6H_4Me-4)(CO)$_2$(η-C_5H_5)] (A = S, Se).[17] Employing a deficiency of chalcogen fails to lead to any isolable chalcogenoacyl complex of the form [W(η^2-ACC_6H_4Me-4)(CO)$_2$(η-C_5H_5)]. It seemed reasonable that steric pressures might partially explain this dichotomy of reactivity; however, this appears not to be the case. Reaction of **1b** with sulfur leads exclusively to the pink dithiobenzoate complex [Mo(κ^2-$S_2CC_6H_3Me_2$-2,6)(CO)$_2$-(η-C_5Me_5)] (**9**), spectroscopic data for which are completely analogous to those reported for [Mo(κ^2-$S_2CC_6H_4$-Me-4)(CO)$_2$(η-C_5H_5)].[17] It therefore appears likely that electronic, rather than steric, effects determine the outcome of this reaction.

Experimental Section

General Procedures. All manipulations were carried out under an atmosphere of prepurified dinitrogen using conventional Schlenk-tube techniques. Solvents were purified by distillation from an appropriate drying agent (ethers and paraffins from sodium/potassium alloy with benzophenone as indicator; halocarbons from CaH_2). ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on either a JEOL GX270 or FX90 NMR spectrometer and calibrated against internal Me_4Si (^1H), internal $CDCl_3$ (^{13}C), or external H_3PO_4 (^{31}P). Infrared spectra were recorded using a Perkin-Elmer 1720-X FT-IR spectrometer. Light petroleum ether refers to that fraction with bp 40–60 °C. Data for the new complexes are given in Tables 1–5.

[W(≡$CC_6H_3Me_2$-2,6)(CO)$_2$(η-C_5Me_5)] (1a). A solution of [W(≡$CC_6H_3Me_2$-2,6)(CO)$_2$(NC_5H_4Me-4)$_2$Br] (10.0 g, 15.2 mmol) in tetrahydrofuran (100 cm^3) was treated with LiC_5Me_5 (2.84 g, 20.0 mmol; from MeLi and C_5Me_5H) and heated under reflux

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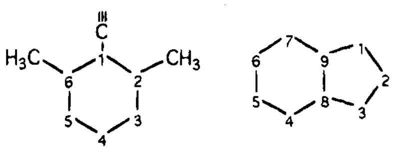
[16] Clark, G. R.; Marsen, K.; Roper, W. R.; Wright, L. J. *J. Am. Chem. Soc.* **1980**, *102*, 6570.

[17] Gill, D. S.; Green, M.; Marsden, K.; Moore, I.; Orpen, A. G.; Stone, F. G. A.; Williams, I. D.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1984**, 1343.

Table 3. Carbon-13 NMR Data[a] for the Complexes



compd	^{13}C (δ)
1a ($CDCl_3$)	299.9 [W≡C, *J*(WC) 212 Hz], 226.4 [WCO, *J*(WC) 195 Hz], 147.8 [C^1 (C_6H_3), *J*(WC) 38 Hz], 139.1, 127.8, 127.1 [C^{2-6} (C_6H_3)], 104.4 [C_5Me_5] 20.6 [$C_6H_3\mathit{Me}_2$], 11.2 [$C_5\mathit{Me}_5$]
1b (CD_2Cl_2)	312.4 [Mo≡C], 234.1 [MoCO], 144.5 [C^1 (C_6H_3)], 140.5, 128.8, 127.5 [C^{2-6} (C_6H_3)], 106.0 [C_5Me_5], 20.8 [$C_6H_3\mathit{Me}_2$], 11.4 [$C_5\mathit{Me}_5$]
1c ($CDCl_3$)	312.5 [Mo≡C], 228.6 [MoCO], 144.0 [C^1 (C_6H_3)], 140.0, 128.8, 127.3 [C^{2-6} (C_6H_3)], 124.3, 122.6 [C^{4-7} (C_9H_7)], 117.3 [$C^{8,9}$ (C_9H_7)], 98.3 [C^2 (C_9H_7)], 78.3 [$C^{1,3}$ (C_9H_7)], 21.0 [$C_6H_3\mathit{Me}_2$]
2a (CD_2Cl_2)	231.9 [WOC*C*$C_6H_3Me_2$, *J*(PC) 8.5, *J* (WC) 167 Hz], 201.6 [WCO, *J*(PC) not resolved], 195.4 [WO*C* $CC_6H_3Me_2$, *J*(PC) not resolved, *J* (WC) 68 Hz], 141.7 [C^1 (C_6H_3)], 131.0, 129.6 [$C^{2,6}$ (C_6H_3)], 126.2, 125.7 [$C^{3,5}$ (C_6H_3)], 124.4 [C^4 (C_6H_3)], 105.0 [C_5Me_5], 20.7, 20.1 [$C_6H_3\mathit{Me}_2$], 18.3 [d, P*Me*$_3$, *J*(PC) 34 Hz], 10.0 [$C_5\mathit{Me}_5$]
2b (CD_2Cl_2)	238.8 [MoOC*C*$C_6H_3Me_2$, *J*(PC) 17.0 Hz], 213.4 [MoCO, *J*(PC) 8.5 Hz], 205.0 [MoO*C*$CC_6H_3Me_2$], 141.2 [C^1 (C_6H_3)], 131.0, 129.2 [$C^{2,6}$ (C_6H_3)], 125.9 [$C^{3,5}$ (C_6H_3)], 124.4 [C^4 (C_6H_3)], 106.1 [C_5Me_5], 20.5, 20.0 [$C_6H_3\mathit{Me}_2$], 17.2 [d, P*Me*$_3$, *J*(PC) 30 Hz], 9.7 [$C_5\mathit{Me}_5$]
3b ($CDCl_3$)	302.4 [d, Mo≡C, *J*(PC) 28 Hz], 242.1 [d, MoCO, *J*(PC) 17.0 Hz], 143.7 [C^1 (C_6H_3)], 137.8, 126.1, 125.9 [C^{2-6} (C_6H_3)], 122.4, 121.9, 121.7 [C^{4-7} (C_9H_7)], 117.3, 115.3[$C^{8,9}$ (C_9H_7)], 95.9 [C^2 (C_9H_7)], 75.8 [$C^{1,3}$ (C_9H_7)], 50.0 [PO*Me*], 20.0 [$C_6H_3\mathit{Me}_2$]
4 ($CDCl_3$)	404.2 [MeFe(μ-C)], 236.0 [MoCO], 212.7 [FeCO], 158.5 [C^1 (C_6H_3)], 126.3 [$C^{3,5}$ (C_6H_3)], 124.8 [C^4 (C_6H_3)], 123.4 [$C^{2,6}$ (C_6H_3)], 107.8 [C_5Me_5], 20.3 [$C_6H_3\mathit{Me}_2$], 9.0 [$C_5\mathit{Me}_5$]
5 ($CDCl_3$)	376.6 [d, MoFe(μ-C)], 253.1 [d, MoFe(μ-CO)], 220.7, 217.7 [MoFe$(CO)_2$], 162.2 [C^1 (C_6H_3)], 140−123 [C_6H_5 and C_6H_3], 105.1 [C_5Me_5], 43.7 [dd, $P_AP_B\mathit{C}H_2$, J(PC) 15, 32 Hz], 23.1, 22.3 [$C_6H_3\mathit{Me}_2$], 10.3 [$C_5\mathit{Me}_5$]
6 ($CDCl_3$)	231.8, 230.8 [MoCO], 211.9 [FeCO], 144.9 [C^1 (C_6H_3)], 136.6, 133.2 [$C^{2,6}$ (C_6H_3)], 129.4 [$C^{3,5}$ (C_6H_3)], 124.4 [C^4 (C_6H_3)], 103.4 [C_5Me_5], 27.4, 23.1 [$C_6H_3\mathit{Me}_2$], 10.5 [$C_5\mathit{Me}_5$]
8b ($CDCl_3$)	319.2 [MoCu(μ-C)], 228.5 [MoCO], 154.7 [C^1 (C_6H_3)], 132.3 [$C^{3,5}$ (C_6H_3)], 128.0 [$C^{2,6}$ (C_6H_3)], 127.0 [C^4 (C_6H_3)], 107.5 [MoC_5Me_5], 93.3 [CuC_5Me_5], 21.8 [$C_6H_3\mathit{Me}_2$], 9.5 [Cu$C_5\mathit{Me}_5$ and Mo$C_5\mathit{Me}_5$]
9 (CD_2Cl_2)	255.1 [MoCO], 237.7 [MoS_2C], 150.3 [C^1 (C_6H_3)], 134.5, 128.8, 127.8, 127.6, 127.0 [C^{2-6} (C_6H_3)], 106.4 [C_5Me_5], 20.3 [$C_6H_3\mathit{Me}_2$], 11.3 [$C_5\mathit{Me}_5$]

[a] Chemical shifts (δ) in ppm, coupling constants in Hz, measurements at room temperature in $CDCl_3$. Spectra are hydrogen-1 decoupled; chemical shifts are positive to high frequency of $SiMe_4$.

Table 4. Mass Spectral Data for Selected Complexes

compd	*m*/*z* (%) [assignt]
1a	492 (57) $[M]^+$, 436 (100) $[M - 2CO]^+$
1b	406 $[M]^+$, 378 $[M - CO]^+$, 438 $[M - 2CO]^+$
2a	524 (1.9) [W($HPCC_6H_3Me_2$)$(CO)_2$(C_5Me_5) ?], 451 (5.7) $[W(CO)_2(PMe_3)(C_5Me_5)]^+$, 423 (3.3) $[W(CO)(PMe_3)(C_5Me_5)]^+$
4	406 (34)$[M - 5CO]^+$, 406 (100) $[M - Fe - 5CO]^+$
5	734 (3.2) $[M - Fe - 3CO]^+$
6	624 (3.5) $[M]^+$, 566 (2.8) $[M - 2CO]^+$, 542 (11.2) $[M - 3CO]^+$, 512 (7.6) $[M - 4CO]^+$
8b	604 (3.0) $[M]^+$, 546 (0.9) $[M\text{-} 2CO]^+$, 469 (3.5) $[M - C_5Me_5]^+$, 438 (2.2) $[M \cdot C_5Me_5 - CO]^+$, 413 (34.1) $[M - C_5Me_5 - 2CO]^+$, 348 $[Mo(CC_6H_3Me_2)(C_5Me_5)]^+$
9	470 (27.0) $[M]^+$, 414 (100) $[M - 2\ CO]^+$, 380 (14.9) $[M - S - 2CO]^+$, 264 (54.4) $[MoSC_5Me_5]^+$

Table 5. Phosphorus-31 NMR Data[a] for the Complexes

compd	^{31}P (δ)
2a	−16.6 [*J*(WP) 397 Hz]
2b	9.6
3a	12.7
3b	198.4
5	41.0 [*J*(AB) 76 Hz] 48.2

[a] Chemical shifts (δ) in ppm, coupling constants in Hz, measurements at room temperature in $CDCl_3$. Spectra are hydrogen-1 decoupled; chemical shifts are positive to high frequency of H_3PO_4.

for 5 h. After the mixture was cooled to room temperature, the solvent was removed under reduced pressure and the residue extracted with a mixture of dichloromethane and light petroleum ether (1:2) and the combined extracts chromatographed on a cryostatically cooled (−40 °C) column loaded with silica gel. Elution with dichloromethane developed a red band, which was freed of solvent in vacuo. The residue was then crystallized from light petroleum ether; yield 5.02 g (67%).

Similar procedures were used for the molybdenum complexes **1b** and **1c**, except that the reaction mixture was not heated but rather, stirred for 18 h. Reaction of [Mo(≡CC_6H_3-Me_2-2,6)$(CO)_2$$(NC_5H_4Me\text{-}4)_2$Br] with LiC_5Me_5 and KC_9H_7 (from potassium and indene) provided the compounds **1b** (yield 4.98 g (70%)) and **1c** (yield 4.26 g (63%)).

[W(η^2-OCC$C_6H_3Me_2$-2,6)(CO)(PMe_3)(η-C_5Me_5)] (2a). A solution of **1a** (1.00 g, 2.03 mmol) in diethyl ether (20 cm^3) was treated with PMe_3 (0.20 g, 2.63 mmol) and the mixture stirred for 12 h. The solvent was removed under reduced pressure and the residue crystallized from a mixture of dichloromethane and light petroleum ether (1:3) at −20 °C; yield 0.97 g (84%). Analogous treatment of **1b** provided **2b**; yield 0.95 g (80%).

[Mo(≡$CC_6H_3Me_2$-2,6)(CO)(PMe_3)(η^5-C_9H_7)] (3a). A solution of **1c** (1.00 g, 2.06 mmol) in diethyl ether (20 cm^3) was treated with PMe_3 (0.20 g, 2.63 mmol) and the mixture was stirred for 6 h. The solvent was removed in vacuo and the residue extracted with a mixture of dichloromethane and light petroleum ether (1:2), and the combined extracts were chromatographed on a cryostatically cooled (−40 °C) column loaded with silica gel. Elution with a mixture of dichloromethane and light petroleum ether (1:2) developed an orange band which was freed of solvent in vacuo. The residue was then crystallized from light petroleum ether; yield 0.74 g (62%). Similar treatment of **1c** with $P(OMe)_3$ provided **3b** (yield 0.87 g (66%)).

[MoFe(μ-$CC_6H_3Me_2$-2,6)$(CO)_5$(η-C_5Me_5)] (4). A mixture of compound **1b** (2.00 g, 4.94 mmol) and $[Fe_2(CO)_9]$ (3.64 g, 10 mmol) in THF (50 cm^3) was stirred for 12 h and then freed of solvent and $[Fe(CO)_5]$ (*Caution*!) in vacuo. The black residue was dissolved in CH_2Cl_2 (10 cm^3), light petroleum ether (10 cm^3) was added, and the solution was chromatographed on an alumina-loaded cryostatically cooled (−20 °C) column. Elution with the same solvent mixture removed a yellow zone ($[Fe(CO)_5]$) and a green zone ($[Fe_3(CO)_{12}]$), which were discarded. Further elution provided a violet fraction from which solvent was slowly removed in vacuo to provide deep violet microcrystals, yield 1.35 g (61%).

[MoFe(μ-$CC_6H_3Me_2$-2,6)$(CO)_3$(μ-dppm)(η-C_5Me_5)] (5). A solution of **4** (1.00 g, 1.84 mmol) in diethyl ether (30 cm^3) was treated with dppm (0.71 g, 1.84 mmol) and the mixture stirred for 10 h, by which time a deep green precipitate had formed. This was isolated by filtration, washed with light petroleum ether, and dried in vacuo; yield 1.43 g (89%).

[MoFe(μ-η^2-$SeCC_6H_3Me_2$-2,6)$(CO)_5$(η-C_5Me_5)] (6). A solution of **4** (0.50 g, 0.92 mmol) in diethyl ether (50 cm^3) was treated with elemental black selenium (0.3 g, excess) and the mixture stirred rapidly for 1 day. The solution was filtered through a plug of diatomaceous earth and then freed of solvent under reduced pressure. The residue was extracted twice with a mixture of CH_2Cl_2 (6 cm^3) and light petroleum ether (14 cm^3). The combined extracts were chromatographed on a water-cooled column with the same solvent mixture as eluent. The major orange band was collected and reduced to ca. 4 cm^3 in vacuo and cooled to −78 °C to provide orange microcrystals of **6**, yield 0.48 g (83%).

[MoCu(μ-$CC_6H_3Me_2$-2,6)$(CO)_2$(η-C_5Me_5)$_2$] (8b). A solution of "Cu(η-C_5Me_5)" (0.50 mmol) in THF prepared according to the literature procedure at −80 °C[15] was treated with **1b** (1.00 g, 0.25 mmol) and the mixture stirred at −80 °C for 24 h and then warmed to room temperature. The solvent was removed in vacuo and the residue extracted with a mixture of dichloromethane and light petroleum ether (1:3). The combined extracts were chromatographed on a cryostatically cooled (−20 °C) column loaded with silica gel. The deep blue band was collected and freed of solvent under reduced pressure. The residue was then crystallized from light petroleum ether at −78 °C; yield 0.90 g (60%).

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