Organometallics 1983, *2*, 1681–1687 1681

Transition-Metal–Cyanocarbon Chemistry. 2. Cyanoacetylene Insertions into the Metal–Hydrogen Bond of (η^5-C_5H_5)(CO)$_3$MH (M = Mo, W) Complexes. Formation of Phosphorus Ylide Complexes and the Structure of (η^5-C_5H_5)(CO)$_2$Mo[η^2-C(CN)PPh$_3$CHCN]

Henri Scordia, René Kergoat, Marek M. Kubicki, and Jacques E. Guerchais*

Laboratoire Associé au CNRS No. 322 (Chimie, Electrochimie et Photochimie Moléculaires), Equipe de Chimie Inorganique Moléculaire, Université de Bretagne Occidentale, 29283 Brest-Cedex, France

Paul L'Haridon

Laboratoire de Chimie Minérale C, Université de Rennes-Beaulieu, 35000 Rennes, France

Received May 5, 1983

Reactions of the hydride complexes (η^5-C_5H_5)(CO)$_3$MH (M = Mo, W) with cyanoacetylene, HC≡CCN, and dicyanoacetylene, NCC≡CCN, in tetrahydrofuran solution gave the corresponding insertion compounds (η^5-C_5H_5)(CO)$_3$M(σ-CR═CHCN) (M = Mo, R = CN; M = W, R = H, CN). Irradiation of these complexes with PPh$_3$ afforded the products (η^5-C_5H_5)(CO)$_2$M(η^2-CRPPh$_3$CHCN) (M = Mo, R = CN; M = W, R = H, CN) containing a phosphorane ligand. Rearrangement of the substitution complex (η^5-C_5H_5)(CO)$_2$PPh$_3$W(σ-CH═CHCN) to (η^5-C_5H_5)(CO)$_2$W(η^2-CHPPh$_3$CHCN) upon irradiation suggests that the formation of ylide complexes from the insertion products may proceed via an initial attack of phosphine on the metal center. (η^5-C_5H_5)(CO)$_2$Mo[η^2-C(CN)PPh$_3$CHCN] has been characterized by an X-ray structure analysis: monoclinic, $P2_1/n$, a = 13.691 (4) Å, b = 15.892 (4) Å, c = 11.557 (5) Å, β = 100.96 (3)°, Z = 4, R = 0.028, R_w = 0.039. This structure, together with the spectroscopic data (IR, ^{1}H and ^{13}C NMR), suggests that the formal negative charge induced by ylide formation is localized on the metal center.

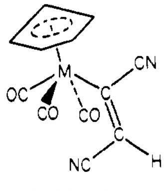
Introduction

The insertion of unsaturated organic molecules into metal–hydrogen bonds is one of the key steps in many homogeneous catalytic systems.[1] Detailed studies of the stoichiometric reactions of alkenes and alkynes with hydrido complexes, thought as relevant models for the intermediates involved in such processes, contribute to a better knowledge of their mechanisms.[2-9] A cursory survey of the literature indicates that surprisingly little has been done in the field of alkynes containing the cyano groups.[5,10,11] The presence of these groups may lead to the formation of stable complexes.[12] Moreover, the nitrile-containing unsaturated molecules exhibit minimal steric effects, thus offering an easy approach to the metallic center.

In view of the above observations, we have undertaken studies of the reactivity of hydrides toward cyano- and dicyanoacetylenes. Our previously observed[13] regio- and stereoselective insertions of these alkynes into each of the two M–H bonds of the complexes (η^5-C_5H_5)$_2$MH$_2$ (M = Mo, W) led us to extend our studies on the monocyclopentadienyl hydrides (η^5-C_5H_5)(CO)$_3$MH (M = Mo, W).

Results and Discussion

Reactions of (η^5-C_5H_5)(CO)$_3$MH (1, M = Mo; 2, M = W) with NCC≡CCN and HC≡CCN. Dicyanoacetylene reacts rapidly with the (η^5-C_5H_5)(CO)$_3$MH complexes causing an immediate color change in the mixture from yellow to dark brown. After removal of the solvent, chromatography of the residue allows the recovery of a small amount of the known binuclear compounds [(η^5-C_5H_5)(CO)$_3$M]$_2$ (**3**, M = Mo; **4**, M = W) and of the yellow products **5** and **6**. The analogous reaction of the tungsten hydride **2** with cyanoacetylene affords a complex (**7**), whereas no defined molybdenum product containing a cyano group could be isolated. The chemical formulations of the new complexes **5** [(η^5-C_5H_5)(CO)$_3$Mo[σ-C(CN)═CHCN)]], **6**, [(η^5-C_5H_5)(CO)$_3$W[σ-C(CN)═CHCN]], and **7**, [(η^5-C_5H_5)(CO)$_3$W(σ-CH═CHCN)] are supported by elemental analytical, IR, and ^{1}H NMR data. The presence of the cyano groups and of the uncoordinated carbon–carbon double bond in the products **5**–**7** is indicated by the occurrence of infrared bands around 2200 and 1500 cm^{-1} (Table I). The ^{1}H NMR spectra of complexes **5** and **6** display singlets in the ethylenic proton region (Table I). The trans geometry around the double bond in **5** and **6** is deduced by comparing their proton chemical shifts with



5, M = Mo
6, M = W

---

(1) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, Calif., 1980. Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978.

(2) Cullen, W. R.; Dawson, D. S.; Styan, G. E. *Can. J. Chem.* **1965**, *43*, 3392.

(3) Harbourne, D. A.; Stone, F. G. A. *J. Chem. Soc. A* **1968**, 1766.

(4) Wailes, P. C.; Weigold, H.; Bell, A. P. *J. Organomet. Chem.* **1971**, *27*, 373.

(5) McClure, G. L.; Baddley, W. H. *J. Organomet. Chem.* **1971**, *27*, 155.

(6) Nakamura, A.; Otsuka, S. *J. Am. Chem. Soc.* **1972**, *94*, 1886.

(7) Nakamura, A.; Otsuka, S. *J. Mol. Catal.* **1975/1976**, *1*, 285.

(8) Davidson, J. L.; Green, M.; Stone, F. G. A.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1976**, 2044.

(9) Laine, R. M.; Ford, P. C. *J. Organomet. Chem.* **1977**, *124*, 29.

(10) McClure, G. L.; Baddley, W. H. *J. Organomet. Chem.* **1970**, *25*; 261.

(11) Dickson, R. S.; Yawney, D. B. W. *Aust. J. Chem.* **1968**, *21*, 1077.

(12) Baddley, W. H. *Inorg. Chim. Acta Rev.* **1968**, 7.

(13) Scordia, H.; Kergoat, R.; Kubicki, M. M.; Guerchais, J. E. *J. Organomet. Chems.* **1983**, *249*, 371.

(14) Petillon, F. Y.; Le Floch-Perennou, F.; Guerchais, J. E.; Sharp, D. W. A.; Manojlović-Muir, Lj.; Muir, K. W. *J. Organomet. Chem.* **1980**, *202*, 23.

0276-7333/83/2302-1681$01.50/0

Table I. Spectroscopic Data

compd	IR, ν (cm^{-1})	^{1}H NMR,^{c} δ	^{13}C NMR,^{c} δ
5, $(\eta^5\text{-}C_5H_5)(CO)_3Mo[\sigma\text{-}C_\alpha(CN){=}C_\beta HCN]$	2220, 2200 (CN) 2060, 1950 (CO) 1520 (C=C)^a	6.55 (s, =CH), 5.60 (s, C_5H_5)	233.7, 224.8 (CO); 149.4 (C_α); 127.6 (C_β); 123.1, 118.0 (CN); 95.5 (C_5H_5)
6, $(\eta^5\text{-}C_5H_5)(CO)_3W[\sigma\text{-}C_\alpha(CN){=}C_\beta HCN]$	2220, 2200 (CN) 2050, 1945 (CO) 1520 (C=C)^a	6.70 (s, =CH), 5.75 (s, C_5H_5)	222.9, 214.1 (CO); 132.5 (C_α); 127.8 (C_β); 123.1, 118.3 (CN); 94.3 (C_5H_5)
7, $(\eta^5\text{-}C_5H_5)(CO)_3W(\sigma\text{-}C_\alpha H_A{=}C_\beta H_B CN)$	2210 (CN) 2040, 1930 (CO) 1525 (C=C)^a	8.70 (d, H_A, $J_{H_A-H_B}$ = 13.5 Hz), 6.45 (d, H_B, $J_{H_A-H_B}$ = 13.5 Hz), 5.70 (s, C_5H_5)	224.7, 214.4 (CO); 155.4 (C_α); 115.4 (C_β); 121.3 (CN); 93.7 (C_5H_5)
8, *trans*-$[(\eta^5\text{-}C_5H_5)(CO)_2PPh_3Mo\{\sigma\text{-}C(CN){=}CHCN\}]$	2210, 2180 (CN) 1960, 1880 (CO) 1510 (C=C)^b	7.30 (m, C_6H_5), 6.72 (s, =CH), 5.00 (d, C_5H_5, J_{P-C} = 1.5 Hz)	
9, $(\eta^5\text{-}C_5H_5)(CO)_2Mo[\eta^2\text{-}C_\alpha(CN)PPh_3C_\beta HCN]$	22100, 2190 (CN) 1915, 1820 (CO)^b	7.50 (m, C_6H_5), 5.33 (s, C_5H_5), 1.50 (d, CH, $^3J_{P-H}$ = 11.5 Hz)	232.4 (d, CO, J_{P-C} = 4.8 Hz); 243.5 (CO); 125.7, 123.0,(CN); 96.3 (C_5H_5); 10.2 (d, C_β, $^2J_{P-C}$ = 3.6 Hz); 1.65 (d, C_α, $^1J_{P-C}$ = 75.2 Hz)
10, $(\eta^5\text{-}C_5H_5)(CO)_2W[\eta^2\text{-}C_\alpha(CN)PPh_3C_\beta HCN]$	2190, 2170 (CN) 1910, 1810 (CO)^b	7.70 (m, C_6H_5), 5.50 (s, C_5H_5), 1.60 (d, CH, $^3J_{P-H}$ = 12.0 Hz)	243.7, 233.3 (CO); 125.9, 123.4 (CN); 95.0 (C_5H_5); 0.12 (C_β); −5.65 (d, C_α, $^1J_{P-C}$ = 73.2 Hz)
11, $(\eta^5\text{-}C_5H_5)(CO)_2W(\eta^2\text{-}C_\alpha H_A PPh_3C_\beta H_B CN)$	2200 (CN) 1880, 1780 (CO)^b	7.70 (m, C_6H_5), 5.35 (s, C_5H_5), 2.40 (dd, H_A, $^3J_{H-H}$ = 6.75 Hz, $^2J_{P-H}$ = 3.75 Hz), 1.20 (dd, H_B, $^3J_{H-H}$ = 6.75 Hz, $^3J_{P-H}$ = 14.40 Hz	243.7 (d, CO, J_{P-C} = 1.2 Hz); 233.7 (CO); 124.3 (CN); 92.2 (C_5H_5); −0.35 (d, C_α, $^1J_{P-C}$ = 63.2 Hz ($^1J_{C-H}$ = 145.9 Hz)^d); −9.9 (C_α ($^1J_{C-H}$ = 164.2 Hz)^d)
12, *trans*-$[(\eta^5\text{-}C_5H_5)(CO)_2PPh_3W(\sigma\text{-}C_\alpha H_A{=}C_\beta H_B CN)]$	2190 (CN) 1965, 1875 (CO) 1510 (C=C)^a	9.00 (d, H_A, $J_{H_A-H_B}$ = 12.5 Hz), 7.50 (m, C_6H_5), 6.42 (d, H_B, $J_{H_A-H_B}$ = 12.5 Hz), 5.05 (d, C_5H_5)	233.6 (d, CO, J_{P-C} = 18.8 Hz); 163.3 (d, C_α, J_{P-C} = 8.3 Hz); 122.8 (CN); 108.9 (d, C_β, J_{P-C} = 4.2 Hz); 92.2 (C_5H_5)

[a] These frequencies were obtained from spectra taken in nujol suspension. [b] These frequencies were obtained from spectra taken in CH_2Cl_2 solution. [c] These spectra were recorded in $CDCl_3$ solution. Multiplicity: s, singlet; d, doublet; dd, double doublet; m, multiplet. [d] This spectrum was recorded on off resonance.

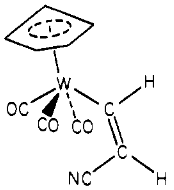
Table II. Chemical Shifts in $CDCl_3$ of σ-Vinylic Protons in Trans and Cis Isomers

compd	δ(^{1}H)	ref
$(\eta^5\text{-}C_5H_5)(CO)_3Mo[\sigma\text{-}C(CN){=}CHCN]$	6.55	this work
$(\eta^5\text{-}C_5H_5)(CO)_3W[\sigma\text{-}C(CN){=}CHCN]$	6.70	this work
Trans Isomers		
$(\eta^5\text{-}C_5H_5)(CO)_3W[\sigma\text{-}$*trans*$\text{-}C(CO_2CH_3){=}CHCO_2CH_3]$	6.47	9
$(\eta^5\text{-}C_5H_5)(CO)_3Mo[\sigma\text{-}$*trans*$\text{-}C(CF_3){=}CHCF_3]$	6.75	14
$(\eta^5\text{-}C_5H_5)(CO)_3W[\sigma\text{-}$*trans*$\text{-}C(CF_3){=}CHCF_3]$	6.82	14
$(\eta^5\text{-}C_5H_5)_2Mo[\sigma\text{-}C(CN){=}CH_2][\sigma\text{-}$*trans*$\text{-}C(CN){=}CH_ACN]$	6.80 (H_A)	13
Cis Isomers		
$(\eta^5\text{-}C_5H_5)(CO)_3W[\sigma\text{-}$*cis*$\text{-}C(CO_2CH_3{=}CHCO_2CH_3]$	6.07	9
$(\eta^5\text{-}C_5H_5)_2Mo[\sigma\text{-}C(CN){=}CH_2][\sigma\text{-}$*cis*$\text{-}C(CN){=}CH_ACN]$	5.96 (H_A)	13

Table III. Selected Interatomic Distances (Å) with Esds for $(\eta^5\text{-}C_5H_5)(CO)_2Mo[\eta^2\text{-}C(CN)PPh_3CHCN]$ (9)

Mo–C(1)	1.947 (3)	C(3)–C(4)	1.488 (4)
Mo–C(2)	1.946 (4)	C(3)–C(6)	1.449 (4)
Mo–C(3)	2.258 (3)	C(4)–C(5)	1.432 (5)
Mo–C(4)	2.225 (3)	C(4)–H(4)	0.911 (39)
Mo–C(51)	2.326 (4)	C(5)–N(1)	1.147 (5)
Mo–C(52)	2.333 (4)	C(6)–N(2)	1.152 (4)
Mo–C(53)	2.348 (4)	P–C(3)	1.802 (3)
Mo–C(54)	2.364 (4)	P–C(1P)	1.793 (3)
Mo–C(55)	2.342 (4)	P–C(2P)	1.803 (3)
C(1)–O(1)	1.164 (4)	P–C(3P)	1.809 (3)
C(2)–O(2)	1.164 (4)		

the positions of the corresponding resonances reported for other complexes that contain σ-vinyl ligands bearing one hydrogen atom (Table II). The values of 6.55 and 6.70 ppm observed for **5** and **6**, respectively, are close to those found for the trans isomers, but they are shifted to lower field than those for the cis isomers. Two doublets, centered at 6.45 and 8.70 ppm, are present in the ^{1}H NMR spectrum of **7**. The corresponding coupling ($^3J_{H-H}$ = 13.5 Hz) is consistent with a double bond having a cis configuration,[3,15] thus indicating formation of a cis-β-metalated compound (**7**).



7

On the basis of the above discussion, it is clear that the insertions of both dicyanoacetylene and cyanoacetylene into the metal–hydride bonds of monocyclopentadienyl complexes proceed in a trans manner. Trans insertion of the NCC≡CCN into the iridium–hydride bond[5] has been established by an X-ray analysis of the compound Ir[σ-C(CN)═CHCN](CO)(NCC≡CCN)$(PPh_3)_2$,[16] and it has been suggested that such trans insertion takes place during the formation of bis(cyclopentadienyl) derivatives $(\eta^5\text{-}C_5H_5)_2MH$[σ-C(CN)═CHCN][13] (M = Mo, W). On the other hand, it has been proposed that there was a cis insertion of the cyanoacetylene into the first M–H bond of the dihydrides $(\eta^5\text{-}C_5H_5)_2MH_2$ (M = Mo, W). A subsequent reaction of the α-metalated complex $(\eta^5\text{-}C_5H_5)_2MoH$[σ-C(CN)═$CH_2$] with HC≡CCN leads to the formation of a cis-β-metalated σ-vinyl ligand (σ-CH═CHCN) via a trans insertion of alkyne into the second Mo–H bond of the initial dihydride. All monocyanoacetylene insertions are regio- and stereoselective, but it seems reasonable to assume that their stereochemistry depends on the electronic structure of the metal. The low electron density of the molybdenum atom in $(\eta^5\text{-}C_5H_5)_2MoH_2$ ($Mo^{VI}\text{-}d^2$) causes it to be bound to a (δ^-) acetylene carbon atom resulting from the polarization of the triple bond $HC^{\delta+}{\equiv}C^{\delta-}CN$. This gives the α-metalated compound $(\eta^5\text{-}C_5H_5)_2MoH$[σ-C(CN)═$CH_2$]. On the other hand, it seems that this last complex and $(\eta^5\text{-}C_5H_5)(CO)_3WH$ are added to HC≡CCN by nucleophilic attack. In the preceding paper[13] we suggested that the insertion of one molecule of HC≡CCN gives rise to an increase in the electron density of molybdenum, enabling it to act as a nucleophilic reagent and thus to behave more like a tungsten hydride (**2**).

It is worth noting that the reactions of molybdenum and tungsten hydrides with NCC≡CCN and HC≡CCN do not give under our experimental conditions any complex containing π-bonded alkynes, known for acetylenes containing electron-withdrawing functional groups, e.g., hexafluorobutyne[8,14] and dimethyl acetylenedicarboxylate.[9] In particular, reactions of hexafluorobutyne with $(\eta^5\text{-}C_5H_5)(CO)_3MH$ (M = Mo, W) afford as sole products the alkyne-bridged binuclear compounds $[(\eta^5\text{-}C_5H_5)(CO)_2M]_2(F_3CC{\equiv}CCF_3)$.[14] This observation can indicate that cyanoacetylenes behave as stronger electrophiles than any of the other activated alkynes and that electron density on molybdenum and tungsten is not sufficiently high to stabilize the π coordination. In fact, the complexes containing π-bonded dicyanoacetylene are know in the case of electron-rich metals (Ir,[5] Pt,[10] Rh,[5] Pd,[5] Co[11]). The strong metal-to-ligand π-back-donation may be responsible of their stability owing to the stabilization of the π-antibonding orbitals of alkyne. It has been suggested recently that the π* orbitals may play an important role in bonding in the transition-metal complexes.[17,18]

Reactions of $(\eta^5\text{-}C_5H_5)(CO)_3M$(σ-CR═CHCN) (M = Mo, R = CN; M = W, R = H, CN) with Triphenylphosphine. Irradiation of a mixture of $(\eta^5\text{-}C_5H_5)(CO)_3Mo$[σ-C(CN)═CHCN] (**5**) and PPh_3 in THF results in the formation of the products **8** and **9**, which can be separated by column chromatography. Spectroscopic data for compound **8** (Table I) are consistent with the formulation $(\eta^5\text{-}C_5H_5)(CO)_2PPh_3Mo$[σ-C(CN)═CHCN] involving the replacement of a carbonyl ligand by the phosphine. The ^{1}H NMR resonance of cyclopentadienyl protons appears as a doublet (J_{P-H} = 1.5 Hz) (Table I). Previous work showed that such a splitting is diagnostic of the trans configuration.[19-22] Complex **9** shows noticeably different spectroscopic features. Its infrared spectrum reveals greater lowering of the carbonyl stretching frequencies (Table I) than would be expected for a product with the phosphine ligand directly bound to the metal atom. In its ^{1}H NMR spectrum, the occurrence of a resonance, split into a doublet (J_{P-H} = 11.5 Hz) at high field (δ 1.50), is significant. This high-field resonance, characteristic of an sp^3-hybridized carbon, indicates a transformation of the σ-vinylic ligand present in **5**. This is confirmed by the ^{13}C NMR spectrum of **9** in which two high-field resonances are observed. One of them is unambiguously assigned to a carbon atom bound to the phosphorus atom $^1J_{P-C}$ = 75.7 Hz).[23] The appearence of the carbonyl resonances in the low-field region of the ^{13}C NMR spectrum (Table I) is not consistent with the presence of the phosphine ligand at the metal center.[24] The reactions of $(\eta^5\text{-}C_5H_5)(CO)_3W$[σ-C(CN)═CHCN] (**6**) and $(\eta^5\text{-}C_5H_5)(CO)_3W$ (σ-CH═CHCN) (**7**) with PPh_3 give $(\eta^5\text{-}C_5H_5)(CO)_2W[\eta^2\text{-}C(CN)\text{-}PPh_3CHCN]$ (**10**) and $(\eta^5\text{-}C_5H_5)(CO)_2W(\eta^2\text{-}CHPPh_3CHCN)$ (**11**), respectively. The spectroscopic features of **11** were of particular interest in establishing the structure of all phosphine-containing compounds **9–11**. Two signals consisting of doublets of doublets, at 2.40 and 1.20 ppm, are observed in the high-field region of the ^{1}H NMR spectrum of **11**. The first splitting is due to a coupling with the vicinal proton ($^3J_{H-H}$ = 6.75 Hz) and the second one to a coupling with the phosphorus atom ($^2J_{P-H}$ = 3.75 Hz, $^3J_{P-H}$ = 14.4 Hz). Two high-field resonances are observed in the ^{13}C NMR spectrum of **11**. The lower field resonance (δ −0.35), recorded as a doublet, is assigned to a carbon atom bound to the phosphine ($^1J_{P-C}$ = 63.2 Hz). The off-resonance spectrum shows that both the corre-

---

(15) Bruce, M. I.; Harbourne, D. A.; Waugh, F.; Stone, F. G. A. *J. Chem. Soc. A* **1967**, 895. Leusink, A. J.; Marsman, J. W.; Budding, H. A.; Noltes, J. G.; van der Kerk, G. J. M. *Recl. Trav. Chim. Pays-Bas* **1965**, *84*, 567. Booth, B. L.; Hargreaves, R. G. J. *J. Chem. Soc. A* **1969**, 2766.

(16) Kirchner, R. M.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 1095.

(17) Tatsumi, K.; Hoffmann, R.; Templeton, J. L. *Inorg. Chem.* **1982**, *21*, 466.

(18) Koie, Y.; Shinoda, S.; Saito, Y. *J. Chem. Soc., Dalton Trans.* **1981**, 1082.

(19) Bainbridge, A.; Craig, P. J.; Green, M. *J. Chem. Soc. A* **1968**, 2715.

(20) Barnett, K. W.; Treichel, P. M. *Inorg. Chem.* **1967**, *6*, 294.

(21) Craig, P. J.; Green, M. *J. Chem. Soc. A* **1968**, 1978.

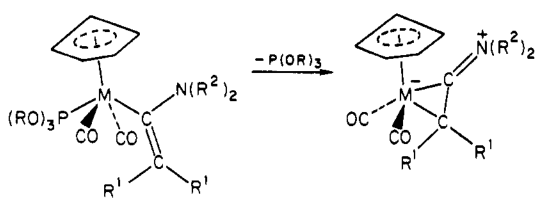
(22) Manning, A. R. *J. Chem. Soc. A* **1967**, 1984.

(23) Yamamoto, Y.; Kanda, Z. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2560.

(24) Todd, L. J.; Wilkinson, J. R.; Phickey, J.; Beach, D. L.; Barnett, K. W. *J. Organomet. Chem.* **1978**, *154*, 151. J_{P-CO} coupling constants in $(\eta^5\text{-}C_5H_5)(CO)_2PR_3MX$ complexes are generally observed in the range of 2–5 Hz and in the range of 20–30 Hz for cis and trans isomers, respectively.

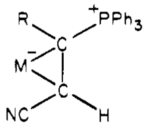
(25) Brix, H.; Beck, W. *J. Organomet. Chem.* **1982**, *234*, 151.

Scheme I



sponding carbon atoms bear a proton.

On the basis of the above observations, the existence of a phosphorus ylide ligand of the type in complexes **9**–**11**



9, M = Mo, R = CN
10, M = W, R = CN
11, M = W, R = H

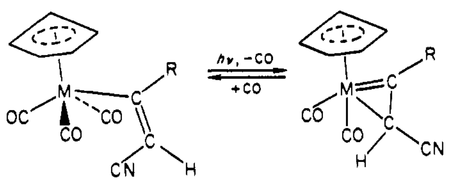
is suggested and confirmed by an X-ray structure determination of **9** (vide infra). Structurally analogous complexes of type $(\eta^5\text{-}C_5H_5)(CO)_2M[\eta^2\text{-}CN(R^2)_2C(R^1)_2]$ (M = Mo, W) have been obtained by Brix and Beck[25] from σ-vinyl compounds $(\eta^5\text{-}C_5H_5)(CO)_2P(OR)_3M[\sigma\text{-}CN(R^2)_2{=}C(R^1)_2]$ (Scheme I). In this case, the easy dissociation of the phosphite ligand may be due to the donor properties of the $\sigma\text{-}CN(R^2)_2{=}C(R^1)_2$ vinylic ligand.

The ylide-type structure explains the more significant spectroscopic features of these three complexes, especially the low ν(CO) infrared frequencies which compare well with those observed for the salts $Me_4N[M^1\{(\eta^5\text{-}C_5H_5\text{-}(CO)_3M^2\}]$ (M^1 = Cu^I, Ag^I; M^2 = Mo, W) containing the $[(\eta^5\text{-}C_5H_5)(CO)_3M^2]^-$ anions.[26] This last feature is consistent with the presence of a negative charge on the metal center associated with the phosphonium ion and reflects increased π-back-bonding (M→CO).

The shielding effect of the cyano groups is particularly obvious if one considers the ^{1}H NMR data of compound **11**. A doublet assigned to H_B (δ 1.20) which is bound to a carbon atom which in turn is substituted with a cyano group occurs at a higher field than that due to H_A (δ 2.40) which is bound to a carbon atom bearing the phosphine (Table I). This shielding effect is also apparent in ^{13}C NMR spectra of **10** and **11**; the replacement of the cyano group bound to the C_α in **10** by a proton in **11** causes the C_α resonance to shift downfield by 5.3 ppm.

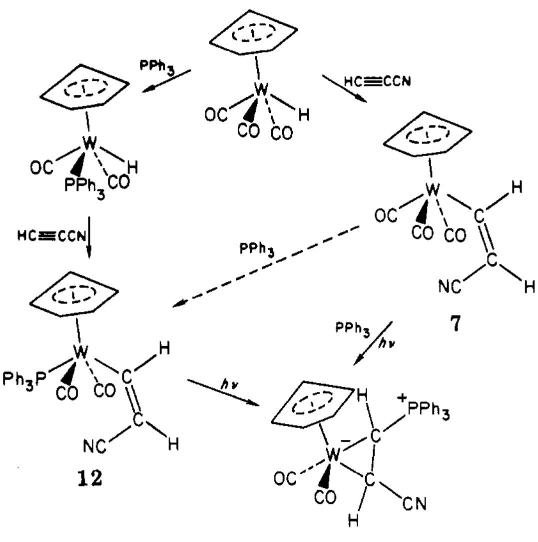
A nucleophilic attack of the phosphine on the σ-vinyl ligand described in this paper contrasts with the behavior of phosphorus nucleophiles toward related complexes of the type $(\eta^5\text{-}C_5H_5)(CO)_3M(\sigma\text{-}R)$ (M = Mo, W; R = alkyl or vinyl). Such an attack consists either of PPh$_3$ substitution for CO[19,20] or of the formation of acyl complexes $(\eta^5\text{-}C_5H_5)(CO)_2MCOR$ without carbonyl loss.[21] Although nucleophilic additions of phosphines to the vinyl ligand of cationic complexes are well documented,[27] examples involving neutral complexes are not numerous and are limited to compounds containing π-bonded alkynes.[28-31]

Scheme II



M = Mo, W; R = H, CN

Scheme III



The question arises as to whether the phosphorane compounds **9**–**11** result from direct attack on a carbon atom or from displacement of one carbonyl group followed by the migration of the coordinated phosphine to the vinyl ligand.

As indicated by ^{13}C NMR data, the α-vinylic carbons in complexes **5**–**7** seem to be fairly electrophilic to undergo the attack of the phosphine. However, the fact that no reaction occurs between the phosphines (PPh$_3$, PMe$_2$Ph, and PMe$_3$) and the diinsertion compound $[(\eta^5\text{-}C_5H_5)_2Mo\{\sigma\text{-}\underline{C}(CN){=}CHCN\}(\sigma\text{-}CH{=}CHCH)]$[32] which contains one strongly deshielded carbon atom (189 ppm for the underlined carbon[13]) argues against the simple admission of such a pathway. A photochemically initiated η^1–η^3 rearrangement of the vinyl ligand to produce a carbene-like complex (Scheme II), then enhancing the possibility of a nucleophilic attack on the α-carbon atom, could explain the observed results, but the NMR study does not give any evidence for the illustrated equilibrium.

On the other hand, irradiation of *trans*-$[(\eta^5\text{-}C_5H_5)(CO)_2PPh_3W(\sigma\text{-}cis\text{-}CH{=}CHCN)]$ (**12**),[21] prepared by the reaction of *cis*-$[(\eta^5\text{-}C_5H_5)(CO)_2PPh_3WH]$[20] with PPh$_3$, gives a phosphorane complex (**11**) in 55% yield. Thus one may assume that the formation of compounds $(\eta^5\text{-}C_5H_5)(CO)_2M(\eta^2\text{-}CRPPh_3CHCN)$ (**9**, **10**, and **11**) from the insertion complexes **5**, **6**, and **7**, respectively, could proceed by a pathway involving initial attack of the phosphine on the metal followed by its intramolecular migration toward

---

(26) Hackett, P.; Manning, A. R. *J. Chem. Soc., Chem. Commun.* **1973**, 71.

(27) See for example ref 8 in ref 37. Kolobova, N. E.; Skripkin, V. V.; Rozantseva, T. V.; Struchkov, Yu. T.; Aleksandrov, G. G.; Andrianov, V. G. *J. Organomet. Chem.* **1981**, *218*, 223. Feser, R.; Werner, H. *J. Organomet. Chem.* **1982**, *233*, 193. Canestrari, M.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1982**, *9*, 1789.

(28) Deeming, A. J.; Hasso, S. *J. Organomet. Chem.* **1976**, *112*, C39.

(29) Kolobova, N. E.; Ivanov, L. L.; Zhvanko, O. S.; Chechulina, I. N.; Batsanov, A. S.; Struchkov, Yu. T. *J. Organomet. Chem.* **1982**, *238*, 223.

(30) Davidson, J. L.; Vasapollo, G.; Manojlović-Muir, Lj.; Muir, K. W. *J. Chem. Soc. Chem. Commun.* **1982**, 1025.

(31) Engelter, C.; Moss, J. R.; Niven, M. L.; Nassimbeni, L. R.; Reid, G. *J. Organomet. Chem.* **1982**, *232*, C78.

(32) Cariou, M.; Kubicki, M. M.; Kergoat, R.; Scordia, H.; Guerchais, J. E., unpublished results.

Table IV. Selected Interatomic Angles (deg) with Esds for (η^5-C_5H_5)(CO)$_2$Mo[η^2-C(CN)PPh$_3$CHCN] (9)

C(1)-Mo-C(2)	76.0 (1)	Mo-C(3)-P	121.9 (1)
C(1)-Mo-C(3)	93.9 (1)	Mo-C(3)-C(4)	69.1 (2)
C(1)-Mo-C(4)	117.4 (1)	Mo-C(3)-C(6)	113.3 (2)
C(2)-Mo-C(3)	108.3 (1)	P-C(3)-C(4)	117.6 (2)
C(2)-Mo-C(4)	84.1 (1)	P-C(3)-C(6)	111.5 (2)
C(3)-Mo-C(4)	38.8 (1)	C(4)-C(3)-C(6)	117.7 (3)
C(1P)-P-C(2P)	110.5 (1)	Mo-C(4)-C(3)	72.1 (2)
C(1P)-P-C(3P)	108.4 (1)	Mo-C(4)-C(5)	115.6 (2)
C(1P)-P-C(3)	110.3 (1)	Mo-C(4)-H(4)	103.4 (2.1)
C(2P)-P-C(3P)	107.4 (1)	C(3)-C(4)-C(5)	118.5 (3)
C(2P)-P-C(3)	109.2 (1)	C(3)-C(4)-H(4)	121.0 (2.5)
C(3)-P-C(3P)	110.9 (1)	C(5)-C(4)-H(4)	120.4 (2.5)

a deshielded carbon atom of the σ-vinylic ligand, as depicted in Scheme III.

A recovery of a small amount of the substitution complex *trans*-[(η_5-C_5H_5)(CO)$_2$PPh$_3$Mo{σ-C(CN)=CHCN}] from the reaction of 5 with PPh$_3$ is in agreement with this pathway. Moreover, the presence of a practically constant amount of **12** all along the photochemical reaction of **7** with PPh$_3$ was observed by monitoring the reaction by ^{1}H NMR.

We note that the tungsten-bond carbon atom in (η^5-C_5H_5)(CO)$_3$W(σ-CH=CHCN) (**7**) undergoes a downfield shift of about 13 ppm on substitution of PPh$_3$ for a carbonyl ligand, complex **12**, thus favoring nucleophilic attack on itself. The importance of the "electrophilic nature" of the σ-vinylic carbon atoms in the formation of ylide complexes is manifested by photochemical reactions of the hexafluorobutyne derivative (η^5-C_5H_5)(CO)$_3$W[σ-C(CF$_3$)=CHCF$_3$] with phosphines and phosphites[33] that afford only the CO substitution products. In fact, it has been shown that irradiation of this derivative leads to rapid formation of (η^5-C_5H_5)(CO)$_2$W[η^3-CO-C(CF$_3$)=CHCF$_3$] containing an η^3-acryloyl ligand that is not able to undergo a nucleophilic addition.

Structure of (η^5-C_5H_5)(CO)$_2$Mo[η^2-C(CN)-PPh$_3$CHCN] (9). An ORTEP drawing showing the molecular structure and atom numbering scheme for (η^5-C_5H_5)(CO)$_2$Mo[η^2-C(CN)PPh$_3$CHCN] is presented in Figure 1. The relevant bond distances and angles are listed in Tables III and IV, The coordination geometry of the molybdenum atom can be described as a distorted, tetragonal pyramid with the cyclopentadienyl ring occupying the apical position. The cyclopentadienyl ring itself is slightly skewed with respect to the molybdenum atom with Mo–C(ring) distances of 2.326, 2.333, 2.348, 2.364, and 2.342 Å for C(51) through C(55), respectively. No evident tilting toward the two carbonyl groups or toward the dicyanophosphorane ligand is manifested by the ring. The Mo–C(carbonyl) distances and OC–Mo–CO angles are normal.

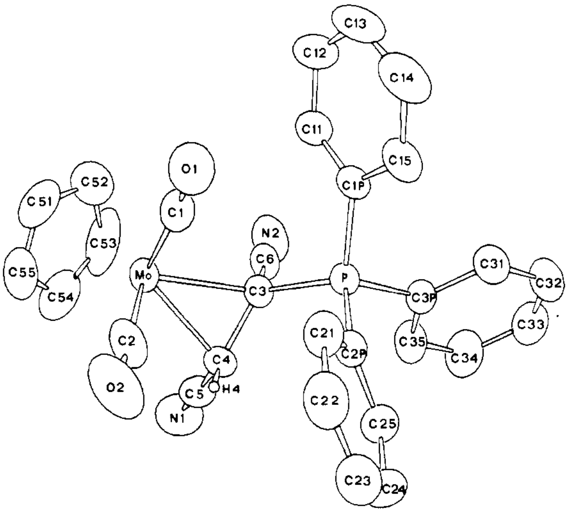


Figure 1. Molecular structure of [(η^5-C_5H_5)(CO)$_2$Mo[η^2-C-(CN)PPh$_3$CHCN] (**9**).

The most interesting feature of the structure is the geometry of the η^2-CH(CN)=C(CN)PPh$_3$ ligand. The P–C(phenyl) bond distances (mean value 1.802 Å) lie in the range of 1.78–1.82 Å, common for the carbon–tetrahedral phosphorus bond. The P–C(3) bond length of 1.802 (3) Å is close to those observed in (η^5-C_5H_5)W-(SCH$_3$)(F$_3$CC≡CCF$_3$)[η^2-C(CF$_3$)PPh$_3$CCF$_3$] (1.810 (5) Å)[30] and in *cis*-[Pt(PPh$_3$)$_2$(CH$_2$PPh$_3$)Cl]I (1.80 (2) Å)[31] but greater than the values found for a P=C double bond (1.640 (6) Å in (CH$_3$)$_3$P=CH$_2$)[34] or for partially double phosphorus–carbon bonds (1.68–1.78 Å),[35] thus indicating the presence of the ylide =C$^-$—P$^+$Ph$_3$ and not the ylene =C=PPh$_3$ resonance form. The C(3)–C(4) bond of 1.488 (4) Å is shorter than the single bond (1.54 Å) but significantly longer than the ethylenic double bond (1.34 Å). This distance lies well between the value of 1.431 (20) Å found in the fumaronitrile complex IrH(CO)-(NCCHCHCN)(PPh$_3$)$_2$[36] and the value of 1.506 (15) Å observed in the iridium tetracyanoethylene complex IrBr(CO)[(NC)$_2$CC(CN)$_2$](PPh$_3$)$_2$.[37] The C–C central bond is longer when bearing four nitrile groups than in the fumaronitrile complex containing two CN groups. In the structure studied here the corresponding distance is significantly longer (3σ) than in the fumaronitrile complex, although both contain two nitrile groups. This suggests that there is a stronger displacement of the electron density flow from the C–C bond toward the central metal atom in **9** than in the fumaronitrile complex. Thus, the formal negative charge induced by ylide formation is localized on the molybdenum atom, as indicated by the spectroscopic study discussed above, rather than on the carbon atoms bearing the nitrile groups. This agrees with suggestions made that ligands with dipolar character, for example, phosphorus[38] or sulfur[39] ylides, as well as imminium zwitterions[40,41] can form remarkably stable transition-metal complexes. The delocalization of charge from the ylidic carbanion onto the metal is of major importance in stabilizing the metal–carbon bond.

The Mo–C distances of 2.258 (3) and 2.225 (3) Å are shorter than the molybdenum–alkyl σ bond lengths of ca. 2.38 Å[42] but much greater than a distance of 1.833 (6) Å

---

(33) Petillon, J. L.; Le Quéré, J. L.; Le Floch-Pérennou, F.; Guerchais, J. E.; Gomes de Lima, M. B.; Manojlović-Muir, Lj.; Muir, K. W.; Sharp, D. W. A. *J. Organomet. Chem.*, submitted for Publication.

(34) Ebsworth, E. A. V.; Fraser, T. E.; Rankin, D. W. H. *Chem. Ber.* **1977**, *110*, 3494.

(35) P–C = 1.679 (4) Å in (CO)$_5$Cr[C$_6$H$_2$(CH$_3$)$_3$PCPh$_2$]: Klebach, T. C.; Lourens, R.; Bickelhaupt, F.; Stam, C. H.; Van Herk, A. *J. Organomet. Chem.* **1981**, *210*, 211. P–C = 1.704 (6) Å in (CO)$_5$W[(CH$_3$S)$_2$CPPh$_2$-(CH$_3$)]: Pickering, R. A.; Jacobson, R. A. Angelici, R. J. *J. Am. Chem. Soc.* **1981**, *103*, 817. P–C = 1.750 (7) Å in (CO)$_5$Cr=C[OSi(CH$_3$)$_3$]CHP-(CH$_3$)$_3$: Voran, S.; Blau, H.; Malisch, W.; Schubert, U. *J. Organomet. Chem.* **1982**, *232*, C33. P–C = 1.761 (3) Å in (η^5-C_5H_5)(CO)$_2$Mn[σ-C-(CO$_2$CH$_3$)=CHPPh$_3$].[26] P–C = 1.779 (6) Å in (η^5-C_5H_5)(CO)$_2$Mn[η^2-PhCH=CHP(O)(OCH$_2$CH$_3$)$_2$]: Antonova, A. B.; Kovalenko, S. V.; Korniyets, E. D.; Johansson, A. A.; Struchkov, Yu. T.; Ahmedov, A. I.; Yanovsky, A. I. *J. Organomet. Chem.* **1983**, *244*, 35.

(36) Muir, K. W.; Ibers, J. A. *J. Organomet. Chem.* **1969**, *18*, 175.

(37) McGinnety, J. A.; Ibers, J. A. *J. Chem. Soc., Chem. Commun.* **1968**, 235.

(38) Schmidbaur, H. *Acc. Chem. Res.* **1975**, *8*, 62.

(39) Koezuka, H.; Matsubayashi, G. E.; Tanaka, T. *Inorg. Chem.* **1974**, *13*, 443.

(40) Carty, A. J.; Taylor, N. J.; Smith, W. F.; Paik, H. N.; Yule, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 41.

(41) Carty, A. J.; Mott, G. N.; Taylor, N. J.; Yule, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 3051.

found in a carbene complex, $(\eta^5\text{-}C_5H_5)[P(OMe)_3]_2ClMo{=}C{=}C(CN)_2$.[43] They are, however, close to the molybdenum–acyl linkage of 2.264 (14) Å in $(\eta^5\text{-}C_5H_5)(CO)_2PPh_3Mo(COMe)$[44] and to the molybdenum-perfluorinated aryl (2.244 (9) Å in $(\eta\text{-}C_7H_7)(CO)_2Mo(\sigma\text{-}C_6F_5)$[45]) or alkyl (2.288 Å in $(\eta^5\text{-}C_5H_5)(CO)_3Mo(\sigma\text{-}C_3F_7)$[46]) bond lengths. The shortening of the molybdenum–carbon bonds relative to a M–C(sp^3) linkage in the presence of electron-withdrawing substituents is thus taken as an indication of d_π–p_π back-donation of electrons from molybdenum to the dicyano phosphorane ligand, i.e., partial multiple bond character in the Mo–C(3) and Mo–C(4) bonds. The shortening of the Mo–C(4) distance with respect to Mo–C(3) may be the consequence either of the effect of bonding of the C(3) atom to a large PPh_3 or of the inequality in the electron density retained on each of the two carbon atoms as indicated by ^{13}C NMR data (Table I). However, the nonbonding Mo–C(5) and Mo–C(6) distances are equal (3.12 and 3.13 Å, respectively). The C–C(nitrile) and C–N bond lengths are normal.[16,36,37]

Final Remark

Considering the fact that a nucleophilic attack by group 5 donors is generally restricted to σ-vinylic ligands of cationic complexes or to the η^2-bonded and simultaneously σ–π-coordinated unsaturated hydrocarbon of the neutral compounds, the phosphorane complexes described in this paper are unique because they result from the bonding of phosphine of the σ-vinylic ligands of the neutral complexes.

Experimental Section

General Remarks. All reactions were performed under a nitrogen atmosphere. Solvents were purified by standard methods and purged with nitrogen before use. Cyanoacetylene and dicyanoacetylene were prepared by the method of Moureu and Bongrand.[47] The complexes $(\eta^5\text{-}C_5H_5)(CO)_3MoH$, $(\eta^5\text{-}C_5H_5)(CO)_3WH$, and $(\eta^5\text{-}C_5H_5)(CO)_2PPh_3WH$ were synthetized by the literature methods.[21,48] All other products were reagent grade materials.

Infrared spectra were recorded on a Pye-Unicam SP 2000 spectrophotometer. NMR spectra were recorded on a JEOL JNM-FX100 spectrometer operating at 99.60 MHz for ^1H and 25.05 MHz for ^{13}C. Chemical shifts were measured relative to an internal reference of $SiMe_4$. Photochemical reactions were run by using a Hanau TQ 150 mercury vapor light.

Preparation of $(\eta^5\text{-}C_5H_5)(CO)_3Mo[\sigma\text{-}C(CN){=}CHCN]$ (5). Mixing $(\eta^5\text{-}C_5H_5)(CO)_3MoH$ (1.5 g, 6.1 mmol) and an excess of dicyanoacetylene (10 mmol) in THF (100 mL) at room temperature gave a dark brown solution that was stirred overnight. Solvent was removed in vacuo, and the residue was dissolved in a minimum of methylene chloride and chromatographed on a "Florisil" column. Elution with a hexane/methylene chloride (1/5) mixture produced a yellow band that gave $(\eta^5\text{-}C_5H_5)(CO)_3Mo[\sigma\text{-}C(CN){=}CHCN)]$ (5) as yellow microcrystals (0.98 g, yield 50% based on $(\eta^5\text{-}C_5H_5)(CO)_3MoH$); mp 105 °C. Anal. Calcd for $C_{12}H_6MoN_2O_3$: C, 44.74; H, 1.88; Mo, 29.78; N, 8.69. Found: C, 44.9; H, 1.9; Mo, 28.7; N, 8.7.

Preparation of $(\eta^5\text{-}C_5H_5)(CO)_3W(\sigma\text{-}CR{=}CHCN)$ (6, R = CN; 7, R = H). Compounds 6 and 7 were prepared in a manner analogous to 5 by adding the appropriate alkyne to a THF solution of $(\eta^5\text{-}C_5H_5)(CO)_3WH$. 6: yield 45%; mp 110 °C. Anal. Calcd for $C_{12}H_6N_2O_3W$: C, 35.15; H, 1.47; N, 6.83; W, 44.83. Found: C, 35.7; H, 1.6; N, 6.7; W, 45.0. 7: yield 55%; mp 118 °C. Anal. Calcd for $C_{11}H_7NO_3W$: C, 34.31; H, 1.83; N, 3.63. Found: C, 34.5; H, 1.8; N, 3.6.

Table V. Crystallographic Data for X-ray Diffraction Study of $(\eta^5\text{-}C_5H_5)(CO)_2Mo[\eta^2\text{-}C(CN)PPh_3CHCN]$ (9)

formula	$C_{29}H_{21}MoN_2O_2P$
space group	$P2_1/n$
a, Å	13.691 (4)
b, Å	15.892 (4)
c, Å	11.557 (5)
β, deg	100.96 (3)
V, Å^3	2468.7
Z	4
ρ(calcd), g cm^{-3}	1.497
abs coeff μ, cm^{-1}	6.096
diffractometer	Enraf-Nonius CAD4
radiation	Mo Kα (λ = 0.710 73 Å)
monochromator	graphite
data limits	$2° \leqslant \theta \leqslant 28°$
total reflctns measd	5194
nonzero data	3453 ($F^2 > 3\sigma(F)^2$)
final residuals	$R = 0.028$ $R_W = 0.039$

Preparation of *trans*-$[(\eta^5\text{-}C_5H_5)(CO)_2PPh_3W(\sigma\text{-}CH{=}CHCN)]$ (12). A reaction mixture containing $(\eta^5\text{-}C_5H_5)(CO)_2PPh_3WH$ (2.1 g, 3.7 mmol) and cyanoacetylene (10 mmol) in THF (100 mL) was stirred at room temperature for 2 days. The solution was taken to dryness under reduced pressure, and the residue, dissolved in a minimum of methylene chloride, was chromatographed on a "Florisil" column. A hexane/methylene chloride (4/1) mixture eluted a yellow band of *trans*-$[(\eta^5\text{-}C_5H_5)(CO)_2PPh_3W(\sigma\text{-}CH{=}CHCN)]$ (12): 1.03 g, yield 45%; mp 240 °C. Anal. Calcd for $C_{28}H_{22}NO_2PW$: C, 54.30; H, 3.58; N, 2.26; P, 5.00; W, 29.58. Found: C, 54.2; H, 3.6; N, 2.2; P, 5.0; W, 29.8.

Preparation of $(\eta^5\text{-}C_5H_5)(CO)_2W(\eta^2\text{-}CHPPh_3CHCN)$ (11). A mixture of $(\eta^5\text{-}C_5H_5)(CO)_3W(\sigma\text{-}CH{=}CHCN)$ (7) (0.88 g, 2.3 mmol) and triphenylphosphine (0.65 g, 2.5 mmol) in THF (60 mL) was irradiated with stirring at room temperature for 24 h. The solvent was removed in vacuo, and the residue was dissolved in a minimum of methylene chloride and chromatographed on a "Florisil" column. Two bands developed. The first, eluted with a hexane/methylene chloride (1/4) mixture, gave the starting material 7. The second, eluted with a methylene chloride/THF (10/1) mixture, afforded the phosphorane complex $(\eta^5\text{-}C_5H_5)(CO)_2W(\eta^2\text{-}CHPPh_3CHCN)$ (11) as bright yellow microcrystals (0.92 g, yield 65%); mp 230 °C. Anal. Calcd for $C_{28}H_{22}NO_2PW$: C, 54.30; H, 3.58; N, 2.26; P, 5.00; W, 29.58. Found: C, 54.4; H, 3.9; N, 2.0; P, 4.5; W, 29.5.

Preparation of $(\eta^5\text{-}C_5H_5)(CO)_2M[\eta^2\text{-}C(CN)PPh_3CHCN]$ (9, M = Mo; 10, M = W). Compounds 9 and 10 were prepared in photochemical reactions analogous to that of 11 by irradiation of mixtures of the phosphine with the appropriate insertion complex 5 or 6. 9: yield 55%; mp 208 °C. Anal. Calcd for $C_{29}H_{21}MoN_2O_2P$: C, 62.60; H, 3.80; Mo, 17.24; N, 5.03; P, 5.57. Found: C, 62.3; H, 3.8; Mo, 16.3; N, 4.8; P, 5.6. 10: yield 50%; mp 223 °C. Anal. Calcd for $C_{29}H_{21}N_2O_2PW$: C, 54.06; H, 3.28; N, 4.35; P, 4.81; W, 28.53. Found: C, 52.2; H, 3.2; N, 4.2; P, 4.1; W, 28.6.

Preparation of $(\eta^5\text{-}C_5H_5)(CO)_2W(\eta^2\text{-}CHPPh_3CHCN)$ (11) by Irradiation of *trans*-$[(\eta^5\text{-}C_5H_5)(CO)_2PPh_3W(\sigma\text{-}CH{=}CHCN)]$ (12). Irradiation of a solution of *trans*-$[(\eta^5\text{-}C_5H_5)(CO)_2PPh_3W(\sigma\text{-}CH{=}CHCN)]$ (12) in THF for 13 h followed by chromatography on a "Florisil" column gave the complex $(\eta^5\text{-}C_5H_5)(CO)_2W(\eta^2\text{-}CHPPh_3CHCN)$ (11) in 55% yield.

Crystallographic Analysis of $(\eta^5\text{-}C_5H_5)(CO)_2Mo[\eta^2\text{-}C(CN)PPh_3CHCN]$ (9). Crystals of 9 suitable for an X-ray diffraction study were obtained by slow evaporation of a benzene/methylene chloride solution at room temperature. A yellow crystal of approximately 0.15 × 0.16 × 0.35 mm per side was mounted on an Enraf-Nonius CAD-4 four-circle diffractometer. Unit cell was determined and refined from 25 randomly selected reflections obtained by using the CAD-4 automatic routines. The space group was identified uniquely from systematic absences observed during data collection. Crystal data and data collection

---

[42] Churchill, M. R. *Perspect. Struct. Chem.* **1971**, *3*, 120.

[43] Kirchner, R. M.; Ibers, J. A.; Saran, M. S.; King, R. B. *J. Am. Chem. Soc.* **1973**, *95*, 5775.

[44] Churchill, M. R.; Fennessey, J. P. *Inorg. Chem.* **1968**, *7*, 953.

[45] Churchill, M. R.; O'Brien, T. A. *J. Chem. Soc. A* **1969**, 1110.

[46] Churchill, M. R.; Fennessey, J. P. *Inorg. Chem.* **1967**, *6*, 1213.

[47] Moureu, C.; Bongrand, J. C. *Ann. Chim.* (*Paris*) **1910**, *9*, 14.

[48] King, R. B. *Organomet. Synth.* **1965**, *1*, 114. King, R. B.; Stone, F. G. A. *Inorg. Synth.* **1963**, *7*, 107.

parameters are listed in Table V. All data processing were performed on a PDP 11/60 computer using the Enraf-Nonius SDP program library.[49] Neutral atom scattering factors and anomalous dispersion corrections applied to all non-hydrogen atoms were those given by Cromer and Waber.[50]

The structure was solved by a combination of Patterson and difference Fourier techniques and refined by full-matrix least-squares methods—the function $\sum w(|F_o| - |F_c|)^2$, $w^{-1} = \sigma_F{}^2 = {}^1/_4(\sigma(I)/(I) + (0.06)^2(I))$,[51] being minimized. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from the final difference Fourier map and refined isotropically. Fractional atomic coordinates, thermal parameters, and structure factor amplitudes are available.[52]

Acknowledgment. We wish to thank Mr. J. Y. Le Gall for recording the NMR spectra.

Registry No. **1**, 12176-06-6; **2**, 12128-26-6; **3**, 12091-64-4; **4**, 12091-65-5; **5**, 87101-95-9; **6**, 87101-96-0; **7**, 87101-97-1; **8**, 87101-98-2; **9**, 87101-99-3; **10**, 87102-00-9; **11**, 87102-01-0; **12**, 87102-02-1; $(\eta^5\text{-}C_5H_5)(Co)_2PPh_3WH$, 33085-24-4; dicyanoacetylene, 1071-98-3; cyanoacetylene, 1070-71-9.

Supplementary Material Available: Tables of final fractional atomic coordinates, thermal parameters, and structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

---

[49] Frentz, B. A. "The Enraf-Nonius CAD4-SDP. A real Time for Concurrent X-ray Data Collection and Crystal Structure Determination"; Schenk, M., Olthof-Hazekamp, R., von Koningsveld, M., Bassi, G. C., Eds.; Delft University Press: Delft, 1978.

[50] Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1975, Vol. IV.

[51] McCaudlish, L. E.; Stout, G. H.; Andrews, L. C. *Acta Crystallogr., Sect. A* **1975**, *A31*, 245.

[52] See supplementary material.

Communications

Regiochemical Control in the Molybdenum-Catalyzed Reactions of Trimethylsilyl- and Ester-Substituted Allylic Acetates

Barry M. Trost* and Mark Lautens

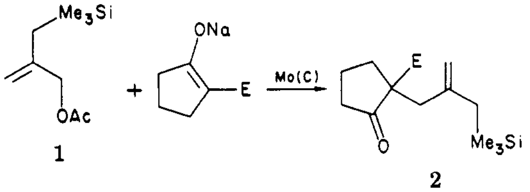
Samuel M. McElvain Laboratories of Organic Chemistry
Department of Chemistry, University of Wisconsin
Madison Wisconsin 53706

Received May 24, 1983

Summary: Molybdenum-catalyzed allylic alkylation performed on allylic acetates also containing allylic or vinylic silanes proceed chemoselectively retaining the silane functionality. For those substrates containing γ-acetoxy α,β-unsaturated esters, both substitution of the allyl acetate and choice of nucleophile allow for complementary regiochemistry.

The transition-metal-catalyzed allylic alkylation offers a new dimension for controlling selectivity in C–C bond formation.[1] Of paramount importance is the question of regiochemical control and the effect of substituents on such a question. The general importance of allyl and vinyl silanes[2,3] and the well-known strong directive effects of electron-withdrawing groups in noncatalyzed reactions led us to examine the trimethylsilyl and carbomethoxy group in molybdenum-catalyzed allylic alkylations.[4] The trimethylsilyl-substituted allyl acetates were of special interest as substrates because of their high propensity to undergo desilylation concomitant with alkylation in palladium-catalyzed reactions.[5]

2-((Trimethylsilyl)methyl)allyl acetate (**1**), the substrate that efficiently loses the elements of trimethylsilyl acetate in the presence of palladium catalysts,[6] became our first target to test the lability of the Me_3Si group in the presence of molybdenum catalysts. Gratifyingly, alkylation of the sodium salt of 2-carbomethoxycyclopentanone gave the simple alkylation product **2** in 60% yield [25% mol% $Mo(CO)_6$, $PhCH_3$, reflux, 72 h] with no trace of a protodesilylated byproduct. The utility of such a product for three carbon intercalation[7] is enhanced due to its easy accessibility from the very stable and easily handled allyl acetate **1** via this molybdenum-catalyzed process. Encouraged by this result, we examined a broader range of trimethylsilyl-substituted allyl acetates with special attention to regioselectivity as summarized in Table I using dimethyl malonate (**3**) and dimethyl methylmalonate (**4**) with 10–20% Mo(c) in refluxing toluene in the presence of *O,N*-bis(trimethylsilyl)acetamide (BSA) as base. The insensitivity of the organosilanes toward desilylation in the Mo-catalyzed reaction in contrast to the Pd-catalyzed reaction is highlighted in entries 2 and 3 in which both an allyl- and vinylsilane survive.



The low regioselectivity in the case of entry 1 is surprising in light of the high regioselectivity for attack at the secondary carbon of crotyl acetate with dimethyl malonate.[8] The increased C–Si bond length compared to a

---

[1] Trost, B. M. *Science (Washington, D.C.)* **1983**, *219*, 245.

[2] Trost, B. M.; Yoshida, J.-I.; Lautens, M. *J. Am. Chem. Soc.*, accepted for publication. Hayashi, T.; Konishi, M.; Ito, H.; Kumada, M. *J. Am. Chem. Soc.* **1982**, *104*, 4962. Hosomi, A.; Iguchi, H.; Sakurai, H. *Chem. Lett.* **1982**, 223. Negishi, E.; Luo, F. T.; Rand, C. L. *Tetrahedron Lett.* **1982**, *23*, 27. Tzeng, D. J.; Weber, W. P. *J. Org. Chem.* **1981**, *46*, 265.

[3] For reviews see: Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761. Sakurai, H. *Pure Appl. Chem.* **1982**, *54*, 1. Fleming, I. *Comp. Org Chem.* **1979**, *3*, 539. Magnus, P. D. *Ibid.* **1982**, *7*, 515.

[4] Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1982**, *104*, 5543.

[5] Trost, B. M.; Self, C. R. *J. Am. Chem. Soc.*, accepted for publication.

[6] Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1979**, *101*, 6429; **1983**, *105*, 2315; 2326.

[7] Cf.: Trost, B. M.; Vincent, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 5680.

[8] Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1983**, *105*, 3343.

[9] For the preparation of the corresponding alcohols see: Tanikaga, R.; Nozaki, Y.; Tamura, T.; Kaji, A. *Synthesis* **1983**, 134; *Chem. Lett.* **1982**, 1703.

0276-7333/83/2302-1687$01.50/0 © 1983 American Chemical Society