ORGANOMETALLICS

Synthesis and reactivity of trans isomers of bis(phosphine)-substituted carbyne complexes of molybdenum and tungsten: [M(.tplbond.CR)X(CO)2(PR3)2]

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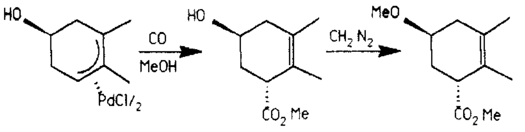
Organometallics, **1987**, 6 (12), 2610-2612• DOI: 10.1021/om00155a030 • Publication Date (Web): 01 May 2002

Organometallics is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

chemistry[16] of the *trans*-(η^3-allyl)palladium complex **2** was confirmed by its transformation to methyl *trans*-5-methoxy-2,3-dimethyl-2-cyclohexene-1-carboxylate (**4**),[17] which was previously obtained by palladium(II)-assisted addition of methanol to 1,2-dimethyl-1,4-cyclohexadiene,[9a] followed by methoxycarbonylation.[9b] Insertion of carbon monoxide into palladium–carbon bonds is known to proceed with complete retention of configuration.[18]



2 **4**

These results[19] corroborate the previous stereochemical studies from Stille's[7] and this laboratory[6] that have provided evidence that distal addition of water and palladium to alkenes, followed by β-elimination of hydride, is the probable mechanism for the Wacker process.

Acknowledgment. We are grateful to the Swedish Board for Technical Development and the Swedish Natural Science Research Council for supporting this research.

Registry No. **2**, 111059-90-6; **3**, 33475-09-1; **4**, 111026-08-5; **5**, 111026-09-6; 1,2-dimethyl-1,4-cyclohexadiene, 17351-28-9; dimethyl malonate anion, 33673-07-3; bis(acetonitrile)palladium chloride, 14592-56-4.

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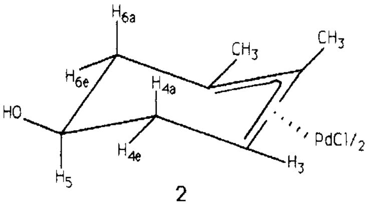
(15) Complex **2**: mp 67–70 °C; IR (KBr) 3390 (br), 2970, 2890, 2820, 1430, 1125, 1040, 995, 925, 780, 730 cm^{-1}; ^{1}H NMR (200 MHz, CDCl$_3$) δ 4.78 (1 H, H-5, apparent quintet, J = ca. 7 Hz), 4.52 (1 H, H-3, t, $J_{3,4a} = J_{3,4e} = 3.3$ Hz), 3.24 (1 H, OH, br s, exchangeable with D$_2$O), 2.43 (1 H, H-6e, dd, $J_{6e,6a} = 15.9$ Hz, $J_{6e,5} = 5.7$ Hz), 2.29 (1 H, H-4e, ddd, $J_{4e,4a} = 15.7$ Hz, $J_{4e,5} = 5.7$ Hz, $J_{4e,3} = 3.7$ Hz), 2.07 (3 H, MeC-2, s), 1.39 (3 H, MeC-1, s) superimposed on 1.34 (1 H, H-6a, dd, $J_{6a,6e} = 15.7$ Hz, $J_{6a,5} = 8.1$ Hz) and 1.24 (1 H, H-4a, ddd, $J_{4a,4e} = 15.1$ Hz, $J_{4a,5} = 7.8$ Hz, $J_{4a,3} = 3.0$ Hz); homonuclear decoupling, irradiation at δ 4.78 collapsed the signals at δ 2.43 and 1.34 to d and at δ 2.29 and 1.24 to dd, irradiation at δ 4.52 collapsed the signals at δ 2.29 and 1.24 to dd, irradiation at ca. δ 2.43 affected the signals at δ 4.78 and 1.34; irradiation at ca. δ 2.29 affected the signals at δ 4.78 and 1.24 and collapsed the signal at δ 4.52 to a d, irradiation at δ 1.30 affected the signals at δ 4.78, 2.43, and 2.29 and collapsed the signal at δ 4.52 to a d; ^{13}C NMR (50 MHz, CDCl$_3$, broadband proton and off-resonance proton decoupling) 113.19 (s), 87.91 (s), 72.26 (d), 65.21 (d), 44.33 (dd), 37.39 (dd), 22.04 (q), 19.08 (q) ppm. Our earlier work on methoxylation[9] has shown that for chair conformations in the (η^3-cyclohexenyl)palladium complexes, the vicinal axial–axial couplings are 7–9 Hz, axial–equatorial couplings are ca. 6 Hz, and the equatorial–equatorial couplings are ca. 2 Hz. The larger (ca. 8 Hz) coupling (axial–axial) between the H-5 proton and the axial protons at C-4 and C-6 and the smaller (5.7 Hz) coupling (axial–equatorial) between the H-5 proton and the equatorial C-4 and C-6 protons establish the conformation of the ring.



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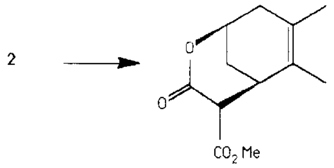
(16) The relative stereochemistry of the palladium complex **2** was also corroborated by its conversion to the lactone **5** with the anion of dimethyl malonate. These alkylations are known to occur directly at carbon on the face of the π-allyl unit opposite the palladium. See: Trost, B. M.; Weber, L. *J. Am. Chem. Soc.* **1975**, *97*, 1611–1612.



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(17) Carboxylate **4**: bp 70 °C (0.08 torr); IR (film) 2970, 2910, 2820, 1727, 1435, 1375, 1360, 1225, 1140, 1090, 960, 840 cm^{-1}; ^{1}H NMR (200 MHz, CDCl$_3$) δ 3.70 (3 H, CO$_2$Me, s), superimposed on 3.77–3.57 (1 H, H-5, complex m), 3.36 (3 H, OMe, s), 3.16 (1 H, H-1, m, $w_{1/2} = 11$ Hz), 2.36 (1 H, H-4e, apparent dd with further fine splitting, $J_{4e,4a}$ = ca. 17 Hz, $J_{4e,5a} = 3.8$ Hz), 2.10 (1 H, H-6e, dddd, $J_{6e,6a} = 12.9$ Hz, $J_{6e,5a} = 5.1$ Hz, $J_{6e,1e} = 3.2$ Hz, $J_{6e,4e} = 1.2$ Hz), 1.96 (1 H, H-4a, dd with further fine splitting, $J_{4a,4e}$ = ca. 17 Hz, $J_{4a,5a}$ = ca. 8 Hz), 1.79 (1 H, H-6a, ddd, $J_{6a,6e} = 12.7$ Hz, $J_{6a,5a} = 9.3$ Hz, $J_{6a,1e} = 6.1$ Hz), and two overlapping Me multiplets with signals at δ 1.67, 1.66, 1.66, 1.65, 1.64 (6 H, MeC-2 and MeC-3); homonuclear decouping, irradiation at δ 3.64 collapsed the signals at δ 2.36 and 1.96 to d and at δ 2.10 and 1.79 to dd, irradiation at δ 3.16 collapsed the signals at δ 2.10 and 1.79 to dd, irradiation at δ 2.36 collapsed the signals at δ 3.77–3.57 to an apparent ddd and at δ 1.96 to a d, irradiation at δ 2.10 collapsed the signals at δ 3.77–3.57 to an apparent ddd, at δ 3.16 to a d, and at δ 1.79 to an apparent dd, irradiation at δ 1.79 collapsed the signals at δ 3.77–3.57 to an apparent ddd, at δ 3.16 to a br s, and at δ 2.10 to an apparent dd; ^{13}C NMR (50 MHz, CDCl$_3$, broad-band proton and off-resonance proton decoupling) 175.53 (s), 127.41 (s), 122.17 (s), 73.40 (d), 55.86 (q), 51.78 (q), 46.19 (d), 37.44 (t), 30.98 (q), 19.60 (q), 17.57 (q) ppm; mass spectrum, m/z (relative intensity) 198 (M$^+$, 2), 167 (11), 166 (100), 139 (38), 125 (19), 107 (94), 106 (19), 91 (45), 79 (23), 58 (28), 45 (28), 41 (30). Anal. Calcd for C$_{11}$H$_{18}$O$_3$: C, 66.64; H, 9.15. Found: C, 66.70; H, 9.10.

(18) Hines, L. F.; Stille, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 485–490.

(19) In contrast to 1,5-cyclooctadiene and norbornadiene (two effective bidentate ligands), 1,4-cyclohexadienes seem to behave essentially as monodentate ligands under these conditions. Only in nonpolar solvents do our NMR studies indicate some coordination by both double bonds of the 1,4-cyclohexadiene. In addition, in some 1,4-cyclohexadienes reactions where the distal addition of methanol was slow, competitive hydride addition was observed.[9b] In these cases, hydride and palladium are adding from the same face, clearly indicating that there is no hindrance to proximal attack. Consequently, substituted 1,4-cyclohexadienes are reasonably acceptable alkene models for the Wacker process.

(20) Åkermark, B.; Hegedus, L. S.; Zetterberg, K.; Olsson, L. F. *J. Am. Chem. Soc.* **1984**, *106*, 7122–7126.

Synthesis and Reactivity of Trans Isomers of Bis(phosphine)-Substituted Carbyne Complexes of Molybdenum and Tungsten: $[M(\equiv CR)X(CO)_2(PR_3)_2]$

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Received June 26, 1987

Summary: Irradiation with visible light of the cis bis(phosphine)-substituted molybdenum and tungsten carbyne complexes *cis,cis*-$[M(\equiv CPh)X(CO)_2(PR_3)_2]$ generates the trans isomers. The isomerization is postulated to proceed via photogenerated pentacoordinate metal ketenyl complexes. Irradiation of *cis,cis*-$[W(\equiv CPh)X(CO)_2(PMe_3)_2]$ at low temperatures in the presence of PMe$_3$ and PhCCH results in formation of the thermally labile tungsten ketenyl complexes $[W(\eta^2\text{-PhCCO})Cl(CO)(PMe_3)_3]$ and $[W(\eta^1\text{-PhCCO})Cl(CO)(PhCCH)(PMe_3)_2]$, respectively. Substitution of one carbonyl ligand in the trans bis(phosphine)-substituted metal carbyne complexes is demonstrated.

Bis(donor ligand)-substituted carbyne complexes of the group 6 transition metals, $[M(\equiv CR)X(CO)_2L_2]$ (M = Cr, Mo, W; X = halide; L = donor ligand),[1] which have become easily available through recently developed new synthetic methods,[2] are generally obtained as the cis L$_2$ derivatives.

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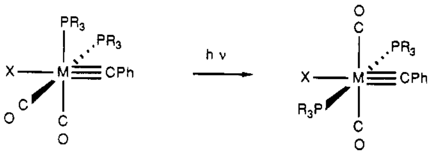
(1) Fischer, E. O.; Ruhs, A.; Kreissl, F. R. *Chem. Ber.* **1977**, *110*, 805–815.

(2) (a) Mayr, A.; McDermott, G. A.; Dorries, A. M. *Organometallics* **1985**, *4*, 608–610. (b) McDermott, G. A.; Dorries, A. M.; Mayr, A. *Organometallics* **1987**, *6*, 925–931.

Formation of a trans-disubstituted isomer has been observed in only one case, $[Cr(\equiv CPh)Br(CO)_2(P(OPh)_3)_2]$.[1] In this molecule the trans isomer is favored by a combination of steric and electronic factors: the small size of the metal center, the steric bulk of the ligand, and the high π-acceptor ability of triphenyl phosphite, which is comparable to that of carbon monoxide.[1] Here we report a general synthesis of trans bis(phosphine)-substituted systems by photoinduced cis–trans isomerization. We discovered this new photoisomerization in the course of efforts to elucidate the nature and reactivity of the emitting state of molybdenum and tungsten carbyne complexes of the type $[M(\equiv CR)X(CO)_2L_2]$, which have previously been shown to luminesce in fluid solution upon irradiation with visible light.[3,4]

Irradiation with visible light of the complexes *cis,cis*-$[M(\equiv CPh)X(CO)_2(PR_3)_2]$ [**1** (M = Mo; X = Br; R = Me),[5] **2** (M = W; X = Cl; R = Me),[2] and **3** (M = W; X = Br; R = Ph)[1]] in organic solvents (tetrahydrofuran, CH_2Cl_2, toluene) effects clean isomerization (by IR) into the compounds *trans,trans*-$[M(\equiv CPh)X(CO)_2(PR_3)_2]$ (**4**, **5**, and **6**, respectively). In a typical procedure the reaction flask (Pyrex glass) is placed into an acetone/dry ice (compound **1**) or ice-water bath (compounds **2** and **3**) and irradiated from a distance of 10–20 cm with a regular 300 projector lamp for approximately 30–60 min. Completion of the reactions is checked by IR. Compound **4** may be recrystallized from diethyl ether, compound **5** from pentane, and compound **6** from CH_2Cl_2/pentane.[6] Compound **4** is thermally labile and air-sensitive. Compounds **5** and **6** are moderately stable and may be handled as solids in air without visible decomposition. For further chemical reactions, however, it is convenient to use freshly prepared solutions. Irradiation of the chromium complex $[Cr(\equiv CPh)Br(CO)_2(PMe_3)_2]$ (**7**)[7] results in loss of carbon monoxide and formation of as yet unidentified products. The bis(pyridine)-substituted compounds *cis,cis*-$[M(\equiv CPh)X(CO)_2(py)_2]$ (M = Cr, Mo, W; X = halide; py = pyridine) do not undergo the photochemical cis–trans isomerization; nevertheless, these compounds exhibit photoreactivity in the presence of added substrates.

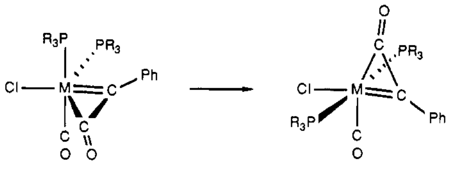


(1)

1: M = Mo; X = Br; R = Me
2: M = W; X = Cl; R = Me
3: M = W; X = Br; R = Ph

4: M = Mo; X = Br; R = Me
5: M = W; X = Cl; R = Me
6: M = W; X = Br; R = Ph

The cis–trans isomerization is believed to proceed via a coordinatively unsaturated intermediate **8** which is generated by coupling of the carbyne ligand with a carbonyl ligand in the excited molecule. Intermediate **8** then isomerizes into a more stable form **9** with the two phosphine ligands in mutual trans positions. Cleavage of the ketenyl ligand in intermediate **9** back into carbyne and carbonyl ligands would then generate the trans isomer. The individual steps of the proposed mechanism are based on precedented reactions. Photoinduced carbonyl–carbyne coupling has previously been observed by Geoffroy[8] and by Fischer.[9] Stereochemical rearrangements occur very easily in five-coordinate transition-metal complexes,[10] and ketenyl ligands are known to cleave back to carbonyl and carbyne ligands.[11] Considering the formal relationship between η^2-ketenyl ligands and four-electron donor alkyne ligands,[12] intermediate **9** is related to trans bis(phosphine)-substituted molybdenum and tungsten alkyne complexes of the type $[MX_2(CO)(R'C\equiv CR')(PR_3)_2]$.[13] The postulated structure of intermediate **9** is derived from this type of alkyne complex by removal of one halide ligand.



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9

Evidence for the nature of photointermediate **9** comes from photoinduced ligand addition reactions. Irradiation of **2** or **5** in CH_2Cl_2 at -78 °C in the presence of trimethylphosphine results in formation of the purple tungsten complex $[W(\eta^2\text{-}PhCCO)Cl(CO)(PMe_3)_3]$ (**10**).[14] The η^2-ketenyl ligand is characterized by an infrared absorption at 1667 cm^{-1} and by two ^{13}C NMR resonances at δ 215 (PhCCO) and 208 (PhCCO). Complex **10** may also be obtained by reaction of **2** with neat trimethylphosphine.[15] Upon warming to room temperature **10** decomposes in solution to $[W(\equiv CPh)Cl(CO)(PMe_3)_3]$,[16] resulting in overall substitution of carbon monoxide in **2** by trimethylphosphine. Irradiation of **2** in CH_2Cl_2 at -78 °C in the presence of excess (5 equiv) phenylacetylene causes a change of color from yellow to deep green. The product is stable only at low temperatures. It was characterized spectroscopically as the η^1-ketenyl alkyne tungsten complex $[W(\eta^1\text{-}PhCCO)Cl(CO)(PhCCH)(PMe_3)_2]$ (**11**).[17] The characteristic data for the η^1-ketenyl ligand

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(3) Bocarsly, A. B.; Cameron, R. E.; Rubin, H.-D.; McDermott, G. A.; Wolff, C. R.; Mayr, A. *Inorg. Chem.* **1985**, *24*, 3976–3978.

(4) Cameron, R. E. Ph.D. Thesis, Princeton University, 1986.

(5) **1**: ^1H NMR (CD_2Cl_2) δ 7.17–7.29 (m, 5 H, Ph), 1.54–1.57 (m, 18 H, $P(CH_3)_3$); ^{13}C NMR (CD_2Cl_2) δ 278.0 (t, J_{CP} = 16.0 Hz, CPh), 215.6 (m, CO); ^{31}P NMR (CD_2Cl_2) δ -20.3 (PMe_3); IR (CH_2Cl_2) ν_{CO} 2008 (s), 1943 (s) cm^{-1}. Complex **1** is synthesized by reaction of $[Mo(CPh)Br(CO)_2(py)_2]$[2] with 2 equiv of PMe_3 in CH_2Cl_2 at 0 °C.

(6) **4**: ^1H NMR (CD_2Cl_2) δ 7.13–7.26 (m, 5 H, Ph), 1.59 (t, 18 H, $P(CH_3)_3$); ^{13}C NMR (CD_2Cl_2) δ 280.9 (t, $^2J_{CP}$ = 15.68 Hz, CPh), 212.6 (t, $^2J_{CP}$ = 10.13 Hz, CO); ^{31}P NMR (CD_2Cl_2) δ -12.7 (s, PMe_3); IR (CH_2Cl_2) ν_{CO} 2006 (vw), 1946 (vs) cm^{-1}. **5**: ^1H NMR ($CDCl_3$, 253 K) δ 7.16 (m, 3 H, Ph), 7.04 (m, 2 H, Ph), 1.07 (t, 18 H, PMe_3); ^{13}C NMR ($CDCl_3$, 253 K) δ 270.5 (t, $^2J_{CP}$ = 9.7 Hz, J_{CW} = 183.1 Hz, CPh), 210 (t, $^2J_{CP}$ = 5.7 Hz, J_{CW} = 125.7 Hz, CO); ^{31}P NMR ($CDCl_3$, 223 K) δ -22.1 (J_{PW} = 273.7 Hz, PMe_3); IR (CH_2Cl_2) ν_{CO} 2018 (vw), 1928 (vs) cm^{-1}. Anal. Calcd for $C_{15}H_{23}ClO_2P_2W$: C, 34.88; H, 4.49. Found: C, 34.74; H, 4.65. **6**: ^1H NMR ($CDCl_3$, 273 K) δ 7.62 (m), 7.28 (m), 7.21 (m, 35 H, $P(C_6H_5)_3$), 6.98 (t), 6.73 (t), 6.26 (d, 5 H, CC_6H_5); ^{13}C NMR ($CDCl_3$, 243 K) δ 271.4 (CPh), 207.9 (CO); ^{31}P NMR ($CDCl_3$, 243 K) δ 19.8 (J_{PW} = 274.3 Hz, PPh_3); IR (CH_2Cl_2) ν_{CO} 2029 (vw), 1937 (vs) cm^{-1}. Anal. Calcd for $C_{45}H_{35}BrO_2P_2W$: C, 57.98; H, 3.78. Found: C, 57.46; H, 3.87.

(7) **7**: ^1H NMR (CD_2Cl_2) δ 7.18–7.32 (m, 5 H, Ph), 1.52–1.55 (m, 18 H, $P(CH_3)_3$); ^{13}C NMR (CD_2Cl_2) δ 302.5 (t, $^2J_{CP}$ = 31.7 Hz, CPh), 226.0 (d, $^2J_{CP}$ = 6.24 Hz, CO); IR (CH_2Cl_2) ν_{CO} 1993 (s), 1933 (s) cm^{-1}. Complex **7** is synthesized by reaction of $[Cr(CPh)Br(CO)_2(py)_2]$[2] with 2 equiv of PMe_3 in CH_2Cl_2 at 0 °C.

(8) Sheridan, J. B.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1986**, *5*, 1514–1515.

(9) Fischer, E. O.; Friedrich, P. *Angew. Chem.* **1979**, *91*, 345–346.

(10) Shapley, J. R.; Osborn, J. A. *Acc Chem. Res.* **1973**, *6*, 305–312.

(11) (a) Eberl, K.; Uedelhofen, W.; Karsch, H. H.; Kreissl, F. R. *Chem. Ber.* **1980**, *113*, 3377–3380. (b) Birdwhistell, K. R.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 4474–4483.

(12) Brower, D. C.; Birdwhistell, K. R.; Templeton, J. L. *Organometallics* **1986**, *5*, 94–98.

(13) (a) Winston, P. B.; Burgmayer, S. J. N.; Tonker, T. L.; Templeton, J. L. *Organometallics* **1986**, *5*, 1707–1715. (b) Davidson, J. L.; Vasapollo, G. *J. Chem. Soc., Dalton Trans.* **1985**, 2239–2245.

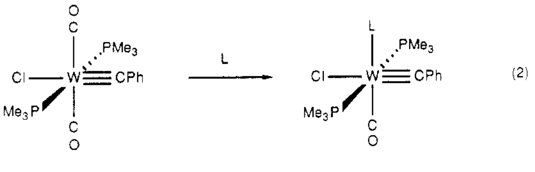
(14) **10**: ^1H NMR (CD_2Cl_2, 213 K) δ 7.14 (m, 5 H, Ph), 1.59 (d, 9 H, PMe_3), 1.41 (t, 18 H, PMe_3); ^{13}C NMR (CD_2Cl_2, 213 K) δ 216.8 (d, t, $^2J_{CP(trans)}$ = 32.6 Hz, $^2J_{CP(cis)}$ = 6.7 Hz, CO), 215.2 (q, $^2J_{CP}$ = 18.2 Hz, PhCCO), 207.9 (PhCCO); IR (CH_2Cl_2) ν_{CO} 1917 (s), ν_{PhCCO} 1667 (w) cm^{-1}.

(15) Complex **10** is a previously unidentified intermediate in the synthesis of $[W(\equiv CPh)Cl(CO)(PMe_3)_3]$.[16]

(16) Mayr, A.; Asaro, M. F.; Kjelsberg, M. A.; Lee, K. S.; Van Engen, D. *Organometallics* **1987**, *6*, 432–434.

are a high-energy infrared stretch at 2015 cm^{-1} and a ^{13}C NMR resonance at δ 172 for the ketenyl carbonyl group. The signal for the terminal ketenyl carbon atom (Ph*C*CO) was not found. The only previously reported ketenyl alkyne metal complex $[W(\eta^5\text{-}C_5H_5)(\eta^1\text{-}p\text{-}MeC_6H_4CCO)(CO)(Et_2NC{\equiv}CMe)]$ was obtained by Kreissl in the the thermal reaction of $[W(\eta^2\text{-}p\text{-}MeC_6H_4CCO)(Cl(CO)(PMe_3)]$ with the alkyne.[18] Complex 11 does not form thermally even by reaction of 2 with neat phenylacetylene.

The trans isomers of the bis(phosphine)-substituted metal carbyne complexes are easily susceptible to substitution of one carbonyl ligand. This increased reactivity compared to the cis isomers is a consequence of the mutual trans orientation of the two π-acceptor carbon monoxide ligands. For example, reaction of complex 5 with trimethylphosphine for 1 h in methylene chloride solution at 40 °C and reaction in neat pyridine for 24 h at room temperature gives the known compounds $[W({\equiv}CPh)Cl(CO)(PMe_3)_3]$[16] and $[W({\equiv}CPh)Cl(CO)(py)(PMe_3)_2]$[16] in 70 and 90% spectroscopic yields, respectively. Reaction of 5 in CH_2Cl_2 with a few drops of concentrated aqueous HCl gives $[W({=}CHPh)Cl_2(CO)(PMe_3)_2]$[16] spectroscopically pure after treatment of the organic phase with Na_2CO_3 and $MgSO_4$.



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L = PMe_3, pyridine

Acknowledgment. This work was supported by the National Science Foundation (CHE 8617472) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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[17] 11: ^1H NMR ($CDCl_3$, 223 K) δ 13.0 (s, 1 H, PhCC*H*), 8.4 (d, 2 H, C_6H_5), 7.5–7.1 (m, C_6H_5), 1.2 (t, 18 H, PMe_3); ^{13}C NMR ($CDCl_3$, 223 K) δ 228.9 (J_{CW} = 132.8 Hz, CO), 208.6 (Ph*C*CH), 203.7 (J_{CH} = 206.6 Hz, PhC*C*H), 172.4 (PhC*C*O), 16.1 (J_{CP} = 14.3 Hz, $P(CH_3)_3$); ^{31}P NMR ($CDCl_3$, 223 K) δ −23.0 (PMe_3); IR (CH_2Cl_2) ν_{PhCCO} 2015 (s), ν_{CO} 1940 (s) cm^{-1}.

[18] Kreissl, F. R.; Reber, G.; Müller, G. *Angew. Chem.* **1986**, *98*, 640–641.

(Pentadienyl)molybdenum Carbonyl Chemistry: Conversion of a Pentadienyl Ligand to a Coordinated Metallabenzene Complex

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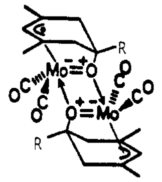
Received July 1, 1987

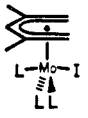
Summary: Reaction of 2 equiv of the (2,4-dimethylpentadienyl)molybdenum tricarbonyl anion with IC_2H_4I leads to the formation of $Mo_2(2,4\text{-}C_7H_{11})(2,4\text{-}C_7H_9)(CO)_5$ which has been characterized spectroscopically and through an X-ray diffraction study. Bonding parameters indicate that a $Mo(2,4\text{-}C_7H_9)$ unit functions as a molybdabenzene fragment η^6 coordinated to the other molybdenum atom.

Recently we reported an entry into (pentadienyl)molybdenum carbonyl chemistry via the $Mo(2,4\text{-}C_7H_{11})(CO)_3$ anion (C_7H_{11} = dimethylpentadienyl).[2] Quite surprisingly, this anion was found to react with methyl iodide to yield an unusual coupling product, 1 (R = CH_3), rather than the expected metal alkyl complex $Mo(2,4\text{-}C_7H_{11})(CH_3)(CO)_3$, cf., $Mo(C_5H_5)(CH_3)(CO)_3$.[3] As there would seem to be a possibility that this type of reaction might have some useful applications, we have examined related reactions designed to probe the generality of this coupling process. In addition to some straightforward transformations, we now report an unusual reaction with diiodoethane, which leads to a product which appears best formulated as an (η^6-metallabenzene)metal complex.



1

The $Mo(2,4\text{-}C_7H_{11})(CO)_3$ anion, readily prepared from $Mo(diglyme)(CO)_3$ and $K(2,4\text{-}C_7H_{11})$, may be easily isolated as crystalline $K(diglyme)^+Mo(2,4\text{-}C_7H_{11})(CO)_3^-$ following toluene extraction.[4] This species undergoes clean reactions with $Hg(CN)_2$, AgI, and I_2, leading to $Hg[Mo(2,4\text{-}C_7H_{11})(CO)_3]_2$, $[Mo(2,4\text{-}C_7H_{11})(CO)_3]_2$, and $Mo(2,4\text{-}C_7H_{11})(I)(CO)_3$ in good yields.[5] All of these complexes have been characterized analytically and spectroscopically, and an X-ray diffraction study of the iodide complex has revealed its configuration to be that of 2.[6]



2

As in the case of methyl iodide, ethyl iodide reacts with $Mo(2,4\text{-}C_7H_{11})(CO)_3^-$ to yield a coupled product (1, R = Et). Reaction with 1,2-diiodoethane, however, yields a product which spectroscopically differs significantly from 1 and furthermore appeared to lack some expected resonances in its NMR spectra. Infrared spectroscopy revealed that all CO ligands were terminally bound, and isopiestic molecular weight determinations indicated a dimetallic structure,[7] but resort to diffraction methods was necessary for a structural assignment.[8]

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[1] (a) University of Utah. (b) University of Delaware.

[2] Kralik, M. S.; Hutchinson, J. P.; Ernst, R. D. *J. Am. Chem. Soc.* **1985**, *107*, 8296.

[3] Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104.

[4] (a) In addition to routine spectroscopic and analytical data, the compound has been characterized by a single-crystal X-ray diffraction study which reveals a polymeric, isocarbonyl complex. (b) Kralik, M. S.; Rheingold, A. L.; Ernst, R. D., unpublished results.

[5] In each case, reactions were carried out in THF at low temperatures and the products subsequently extracted with hexane after THF removal in vacuo. Yields were 90%, 45%, and 60%, respectively. Experimental details and spectroscopic data for all compounds are included in the supplementary material.

[6] (a) Unfortunately, the structure was subject to an apparent disorder, possibly the result of a twinned crystal. (b) Rheingold, A. L., unpublished results.

[7] Calculated molecular weight (isopiestic, THF): 520. Found: 530. Anal. Calcd for $C_{19}H_{20}Mo_2O_5$: C, 43.87; H, 3.87. Found: C, 44.38; H, 4.12. IR (pentane solution, CO region): 2037 (s), 1996 (s), 1942 (m), 1928 (s), 1907 (s) cm^{-1}. Melting point: 142–144 °C.

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