Organometallics **1998,** *17,* 3733−3738

New Procedure for the Synthesis of (Fulvalene)ditungsten Carbonyl Halides and Cyclopentadienyltungsten Carbonyl Halide Complexes with P-Donor Nucleophiles

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Received March 11, 1998

The reactions of (η^5:η^5-$C_{10}H_8$)$W_2(CO)_6I_2$ and (η^5-C_5H_5)$W(CO)_3I$ with P-donor nucleophiles (L = $P(OMe)_3$, $PPhMe_2$, P(n-Bu)$_3$, PPh_2Me, P(p-tol)$_3$, P(m-tol)$_3$, and PCy_3) in the presence of 2 and 1 equiv, respectively, of Me_3NO yield (η^5:η^5-$C_{10}H_8$)$W_2(CO)_4L_2I_2$ and (η^5-C_5H_5)$W(CO)_2$-LI, respectively, as a mixture of *cis*/*trans* isomers. The relative proportion of these isomers is dependent of the stereoelectronic properties of the phosphine ligands. The X-ray structure of (η^5:η^5-($C_{10}H_8$)$W_2(CO)_6I_2$ has been determined.

Introduction

Organometallic compounds that incorporate two or more reactive metal sites in close proximity might provide access to reaction pathways not available to mononuclear systems as a result of cooperative electronic and/or steric effects.[1]

In contrast to the well-studied cyclopentadienylmetal carbonyl dimers, the fulvalene-bridged analogues are expected to show, and have shown in several cases, enhanced reactivity. This is due, in part, to the ability of the fulvalene ligand to allow for metal−metal bond cleavage while inhibiting fragmentation to mononuclear complexes; the potential for metal−metal cooperativity is maintained through relative proximity and possibly by communication through the π-bond system of the fulvalene ligand.[2]

The chemistry of the (η^5:η^5-$C_{10}H_8$)$W_2(CO)_6$ complex has been relatively unexplored[3] in comparison with the molybdenum analogues.[4] Unfortunately, direct substitutions of the CO ligands with tertiary phosphines do not generally ocurr,[3,4] in contrast to the cyclopentadienylmetal carbonyl dimers, (η^5-C_5H_5)$_2W_2(CO)_6$, which may yield P-donor substituted W−W-bonded dimers (η^5-C_5H_5)$_2W_2(CO)_{6-x}(PR_3)_x$ ($x = 1, 2$)[5] or disproportionation products [(η^5-C_5H_5)$W(CO)_2(PR_3)_2^+$][(η^5-C_5H_5)$W(CO)_3^-$],[6] depending on reaction conditions and the electronic and steric properties of PR_3.

However, is known that (η^5:η^5-$C_{10}H_8$)$M_2(CO)_6$ (M = Mo, W) complexes react directly with strongly donating phosphines, to give the zwitterionic compounds (η^5:η^5-$C_{10}H_8$)$M_2(CO)_5L_2$ (L = PMe_3, dmpm),[3] and halo compounds of the type (η^5-C_5H_5)$W(CO)_2LI$ and (η^5:η^5-$C_{10}H_8$)-$Mo_2(CO)_4L_2X_2$ (L = phosphines) (X = Cl, Br, I) have been prepared by direct substitution of a CO ligand from the parent dihalides with a phosphine ligand.[7]

In this paper we report the reactions of (η^5-C_5H_5)W-$(CO)_3I$ and (η^5:η^5-$C_{10}H_8$)$W_2(CO)_6I_2$ with a wide variety of P-nucleophiles with different stereoelectronic properties, in order to evaluate the influence of the fulvalene ligand on the reactivity, and we describe a general method for synthesis of phosphine-substituted (fulvalene)dimetal carbonyl halide complexes.

Experimental Section

Reagents and General Techniques. All manipulations were carried out by using standard Schlenk vacuum-line and syringe techniques under an atmosphere of oxygen-free Ar. All solvents for synthetic use were reagent grade. Diglyme, pentane, tetrahydrofuran (THF), diethyl ether, and hexane were dried and distilled over sodium in the presence of benzophenone ketyl under an Ar atmosphere. Also under Ar atmosphere, carbon tetrachloride, dichloromethane (DCM), dichloroethane (DCE), and toluene were dried and distilled over $MgSO_4$, CaH_2, and sodium, respectively. All solvents were

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(1) (a) Muetterties, E. L.; Rhodin, R. N.; Band, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91. (b) Marks, T. J. *Acc. Chem. Res.* **1992**, *25*, 57. (c) Süss-Fink, G.; Meister, G. *Adv. Organomet. Chem.* **1993**, *35*, 41.

(2) Desbois, M. H.; Astruc, D.; Guillin, J.; Maiot, J. P.; Varret, F. *J. Am. Chem. Soc.* **1985**, *107*, 5280.

(3) (a) Tilset, M.; Vollhardt, K. P. C.; Boese, R. *Organometallics* **1994**, *13*, 3146. (b) Tilset, M.; Vollhardt, K. P. C. *Organometallics* **1985**, *4*, 2230.

(4) Drage, J. S.; Vollhardt, K. P. C. *Organometallics* **1986**, *5*, 280.

(5) (a) Barnett, K. W.; Treichel, P. M. *Inorg. Chem.* **1967**, *6*, 294. (b) King, R. B.; Pannell, K. H. *Inorg. Chem.* **1968**, *7*, 2356. (c) Haines, R. J.; Nyholm, R. S.; Stiddard, M. H. B. *J. Chem. Soc. A* **1968**, 43. (d) Haines, R. J.; Marais, I. L.; Nolte, C. R. *J. Chem. Soc., Chem. Commun.* **1970**, 547. (e) Haines, R. J.; Nolte, C. R. *J. Organomet. Chem.* **1970**, *24*, 725. (f) Haines, R. J.; Du Preez, A. L.; Marais, I. L. *J. Organomet. Chem.* **1971**, *28*, 97.

(6) For reviews with extensive references to reactions between $Cp_2M_2(CO)_6$ and phosphines see: (a) Tyler, D. R. In *Organometallic Radical Processes*; Trogler, W. C., Ed.; Elsevier: New York 1990; p 338. (b) Tyler, D. *Prog. Inorg. Chem.* **1988**, *36*, 125.

(7) (a) Treichel, P. M.; Barnett, K. W.; Shubkin, R. L. *J. Organomet. Chem.* **1967**, *7*, 449. (b) Kovács, I.; Baird, M. C. *Organometallics* **1995**, *14*, 4074.

S0276-7333(98)00180-0 CCC: $15.00
Publication on Web 07/30/1998

bubbled with Ar for 1 h after distillation and then stored under Ar or degassed by means of at least 3 freeze−pump−thaw cycles after distillation and before use.

The compounds $[(\eta^5\text{-}C_5H_5)W(CO)_3]_2$,[8] $(\eta^5\text{-}C_5H_5)W(CO)_3I$[9] (**1**), $(\eta^5{:}\eta^5\text{-}C_{10}H_8)W_2(CO)_6$,[10] $(\eta^5{:}\eta^5\text{-}C_{10}H_8)W_2(CO)_6I_2$[3] (**2**), and $(\eta^5\text{-}C_5H_5)W(CO)_2(PCy_3)I$[11] were prepared according to literature procedures. The halo derivatives were purified by thin-layer chromatography (TLC) using CH_2Cl_2/hexane (1:2) as eluent. Trimethylamine *N*-oxide (Aldrich) was sublimed prior to use and stored under argon. The ^{1}H NMR spectra were recorded on a Bruker AMX-300 or -500 instrument. Chemical shifts were measured relative to an internal reference of tetramethylsilane or to residual protons of the solvents for ^{1}H and H_3PO_4 for ^{31}P. Infrared spectra were measured on a Perkin-Elmer 1650 infrared spectrometer. Elemental analyses were performed by the Mycroanalytical Laboratory of the University Autónoma of Madrid on a Perkin-Elmer 240 B microanalyzer. Electronic spectra were recorded on a Pye Unicam SP 8-100 UV−visible spectrophotometer. Mass spectra were measured on a VG-Autospec mass spectrometer for FAB or AIE by the Mass Laboratory of the University Autónoma of Madrid.

Preparation of $(\eta^5\text{-}C_5H_5)W(CO)_2LI$ (L = $P(OMe)_3$ (3), $PPhMe_2$ (4), $P(n\text{-}Bu)_3$ (5), PPh_2Me (6), $P(p\text{-}tol)_3$ (7), $P(m\text{-}tol)_3$ (8), and PCy_3 (9)). Separation of Two Isomers. Method A. These compounds were synthesized by a modification of the literature method[7a] previously described for $(\eta^5\text{-}C_5H_5)W(CO)_2(PCy_3)I$.[11] A solution of L (0.18 mmol) in THF (15 mL) was added to a solution of $(\eta^5\text{-}C_5H_5)W(CO)_3I$ (0.05 g, 0.11 mmol) in the same solvent (30 mL). The solutions were refluxed for a period of 1−7 days to produce a mixture of *cis* and *trans* isomers. The reactions were monitored by FTIR spectroscopy. Upon filtration and removal of the solvent under reduced pressure, reddish-brown solids were obtained which were extracted with DCM, and the *cis* and *trans* mixtures were separated and purified by TLC using DCM/hexane (1:2) as eluent.

3. Yield: 65%. *Cis*:*trans* isomer ratio: 10:90%. IR (THF): ν_{CO} 1964 (m), 1886 (vs) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): *cis* δ 5.53 (s, 5H), 3.70 (s, 9H); *trans* δ 5.39 (d, 5H, J_{PH} 2.0 Hz), 3.70 (s, 9H). ^{31}P ($CDCl_3$): *cis* 134.16 (s); *trans* 146.67 (s). Anal. Calcd for $C_{10}H_{14}WO_5PI$: C, 21.60; H, 2.54. Found: C, 21.39; H, 2.68.

4. Yield: 63%. *Cis*:*trans* isomer ratio: 25:75%. IR (THF): ν_{CO} 1947 (s), 1861 (vs) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): *cis* δ 5.41 (s, 5H), 7.75 (m, 2H, *o*-Ph), 7.55 (m, 3H, *m*-Ph and *p*-Ph), 2.10 (m, 6H_{cis}), *trans* δ 5.28 (d, 5H, J_{PH} 2.3 Hz,), 7.75 (m, 2H, *o*-Ph), 7.55 (m, 3H, *m*-Ph and *p*-Ph), 1.94 (d, 6H_{trans} J_{PH} 13.1 Hz). ^{31}P ($CDCl_3$): *cis* 26.21 (s); *trans* 34.46 (s). Anal. Calcd for $C_{15}H_{16}WO_2PI$: C, 31.61; H, 2.83. Found: C, 30.90; H, 2.95.

5. Yield: 55%. *Cis*:*trans* isomer ratio: 60:40%. IR (THF): ν_{CO} 1946 (vs), 1856 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): *cis* δ 5.48 (s, 5H), 1.56 (s, 6H), 1.43 (s, 12H), 0.96 (s, 9H); *trans* δ 5.27 (d, 5H, J_{PH} 1.9 Hz), 1.56 (s, 6H), 1.43 (s, 12H), 0.96 (s, 9H). ^{31}P ($CDCl_3$): *cis* 49.82 (s); *trans* 58.25 (s). Anal. Calcd for $C_{19}H_{32}WO_2PI$: C, 35.98; H, 5.09. Found: C, 35.44; H, 5.12.

6. Yield: 60%. *Cis*:*trans* isomer ratio: 80:20%. IR (THF): ν_{CO} 1950 (vs), 1870 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): *cis* δ 5.37 (s, 5H), 7.75 (m, 4H, *o*-Ph), 7.51 (m, 6H, *m*-Ph and *p*-Ph), 1.60 (s, 3H); *trans* δ 5.08 (d, 5H, J_{PH} 2.1 Hz), 7.75 (m, 4H, *o*-Ph), 7.51 (m, 6H, *m*-Ph and *p*-Ph), 1.60 (s, 3H). ^{31}P ($CDCl_3$): *cis* −4.68 (s); *trans* 10.65 (s). Anal. Calcd for $C_{20}H_{18}WO_2PI$: C, 38.00; H, 2.87. Found: C, 37.25; H, 2.95.

7. Yield: 50%. *Cis*:*trans* isomer ratio: 30:70%. IR (THF): ν_{CO} 1948 (s), 1874 (vs) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): *cis* δ 5.45 (s, 5H), 7.55 (m, 6H, *o*-Ph), 7.19 (m, 6H, *m*-Ph), 2.34 (s, 3H).); *trans* δ 5.12 (d, 5H, J_{PH} 1.9 Hz), 7.55 (m, 6H, *o*-Ph), 7.19 (m, 6H, *m*-Ph), 2.34 (s, 3H). ^{31}P ($CDCl_3$): *cis* 28.70 (s); *trans* 29.78 (s). Anal. Calcd for $C_{28}H_{26}WO_2PI$: C, 45.68; H, 3.56. Found: C, 44.85; H, 3.79.

8. Yield: 60%. *Cis*:*trans* isomer ratio: 40:60%. IR (THF): ν_{CO} 1949 (s), 1875 (vs) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): *cis* δ 5.44 (s, 5H), 7.33 (m, 12H, Ph), 2.35 (s, 9H); *trans* δ 5.11 (d, 5H, J_{PH} 1.8 Hz) 7.33 (m, 12H, Ph), 2.35 (s, 9H). ^{31}P ($CDCl_3$): *cis* 24.59 (s); *trans* 29.96 (s). Anal. Calcd for $C_{28}H_{26}WO_2PI$: C, 45.68; H, 3.56. Found: C, 45.22; H, 3.89.

9. Yield: 98%. *Cis*:*trans* isomer ratio: 95:5%. IR (THF): ν_{CO} 1940 (vs), 1859 (m) cm^{-1}.

Method B. These compounds are also accessible in higher yields (95%, 93%, 96%, 90%, 80%, 90%, and 99% respectively) by the same procedure used in the preparation of $(\eta^5{:}\eta^5\text{-}(C_{10}H_8)\text{-}W_2(CO)_6L_2I_2$ complexes.

Preparation of $(\eta^5{:}\eta^5\text{-}C_{10}H_8)W_2(CO)_4L_2I_2$ (L = $P(OMe)_3$ (10), $PPhMe_2$ (11), PPh_2Me (12), and PCy_3 (13)). Trimethylamine *N*-oxide was utilized to chemically oxidize and remove two CO molecules. The same procedure was followed in the preparation of all phosphine-substituted (fulvalene)-ditungsten carbonyl halide complexes. Solutions of 0.12 g (0.13 mmol) of $(\eta^5{:}\eta^5\text{-}C_{10}H_8)W_2(CO)_6I_2$ and 0.26 mmol of L in 25 mL of THF were prepared. Trimethylamine *N*-oxide (0.0198 g, 0.26 mmol) was added with vigorous magnetic stirring. The solutions were stirred until the reactions were seen to be completed by IR spectroscopy. After ~10 min, no starting material remained; the reddish-brown solid was extracted with DCM and purified by TLC using DCM/hexane (1:2) as eluent. Solvent removal followed by recrystallization (CH_2Cl_2−hexane, at −20 °C) afforded red-brown crystalline products.

10. Yield: 90%. IR (THF): ν_{CO} 1964 (s), 1885 (vs) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.89 (m, Fv), 5.87 (m, Fv), 5.85 (m, Fv), 5.82 (m, Fv), 5.07 (m, Fv), 5.05 (m, Fv), 4.63 (m, Fv), 4.58 (m, Fv), 4.44 (m, Fv), 4.40 (m, Fv), 3.67 (s, 9H). ^{31}P ($CDCl_3$): 146.72 (s, *trans*−*trans*), 145.50 (s, *cis*−*trans*), 133.21 (s, *cis*−*trans*), 134.80 (s, *cis*−*cis*). Anal. Calcd for $C_{20}H_{26}W_2O_{10}P_2I_2$: C, 21.64; H, 2.36. Found: C, 21.50; H, 2.47.

11. Yield: 96%. IR (THF): ν_{CO} 1947 (s), 1863 (vs) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.07 (m, Fv), 5.98 (m, Fv), 5.86 (m, Fv), 5.42 (m, Fv), 5.24 (m, Fv), 5.06 (m, Fv), 5.03 (m, Fv), 5.00 (m, Fv), 4.85 (m, Fv), 4.53(m, Fv), 7.75 (m, 2H, *o*-Ph), 7.50 (m, 3H, *m*-Ph and *p*-Ph), 2.53 (m, H_{cis}), 2.23 (m, H_{cis}), 1.96 (d, H_{trans}, J_{PH} 13.1 Hz). ^{31}P ($CDCl_3$): 34.72 (s, *trans*−*trans*), 33.10 (s, *cis*−*trans*), 25.90 (s, *cis*−*trans*), 24.50 (s, *cis*−*cis*). Anal. Calcd for $C_{30}H_{30}W_2O_4P_2I_2$: C, 31.66; H, 2.66. Found: C, 31.52; H, 2.72.

12. Yield: 97% . IR (THF): ν_{CO} 1950 (vs), 1866 (s) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.80 (m, 2H, ring-4), 5.75 (m, 2H, ring-5), 5.27 (m, 1H, ring-2), 5.20 (m, 2H, ring-5), 5.16 (m, 4H, ring-4 and -5), 5.12 (m, 2H, ring-4), 5.01 (m, 2H, ring-5), 4.95 (m, 5H, ring-1 and -3), 4.91 (m, 1H, ring-3), 4.89 (m, 3H, ring-2 and -4), 4.76 (m, 2H, ring-5), 4.72 (m, 4H, ring-1), 4.69 (m, 1H, ring-3), 4.58 (m, 1H, ring-3), 7.47 (m, 32H, *o*-Ph), 7.39 (m, 48H, *m*-Ph and *p*-Ph), 2.51 (s, Me), 2.48 (d, Me), 2.46 (s, Me), 2.41 (d, Me), 2.36 (s, Me), 2.33 (s, Me). ^{31}P ($CDCl_3$): 10.40 (s, *trans*−*trans*), 10.13 (s, *cis*−*trans*), −4.44 (d, *cis*−*cis meso* and *dl*), −4.61 (s, *cis*−*trans*). Anal. Calcd for $C_{40}H_{34}W_2O_4P_2I_2$: C, 38.06; H, 2.72. Found: C, 37.93; H, 2.84.

13. Yield: 95%. IR (THF): ν_{CO} 1941 (vs), 1858 (s) cm^{-1}. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 5.85 (m, Fv), 5.82 (m, Fv), 5.53 (m, Fv), 5.44 (m, Fv), 5.39 (m, , Fv), 5.25 (m, Fv), 5.21 (m, Fv), 4.71 (m, Fv), 1.43 (m, Cy), 1.89 (m, Cy). ^{31}P (CD_2Cl_2): 52.30 (s, *cis*−*cis meso* and *dl*). Anal. Calcd for $C_{50}H_{74}W_2O_4P_2I_2$: C, 42.22; H, 5.24. Found: C, 42.09; H, 5.36.

X-ray Diffraction Analysis of $(\eta^5{:}\eta^5\text{-}C_{10}H_8)Mo_2(CO)_6I_2$ (2). Orange, plate-shaped crystals of $(\eta^5{:}\eta^5\text{-}C_{10}H_8)W_2(CO)_6I_2$, **2**, are obtained by recrystallization of the complex from CH_2Cl_2/hexane mixtures. Intensity data were collected on a Siemens P4 diffractometer using graphite-monochromated Mo

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(8) Birdwhistell, R.; Hackett, P.; Manning, A. R. *J. Organomet. Chem.* **1978**, *157*, 239.

(9) Abel, E. W.; Singh, A.; Wilkinson, G. *J. Chem. Soc.* **1960**, 1321.

(10) Vollhard, K. P. C.; Weidman, T. W. *Organometallics* **1984**, *3*, 82.

(11) Marcos, M. L.; Moreno, C.; Macazaga, M. J.; Medina R. M.; Maderuelo, R.; Delgado, S.; González-Velasco, J. *J. Organomet Chem.* **1998**, *555*, 57.

Table 1. Crystal Data and Structure Refinement for 1

empirical formula	$C_{16}H_8I_2O_6W_2$
fw	917.72
temp	173(2) K
wavelength	0.710 73 Å
cryst system	triclinic
space group	$P\bar{1}$
unit cell dimens	$a = 7.063(7)$ Å, $\alpha = 82.14(8)°$ $b = 7.789(7)$ Å, $\beta = 85.97(8)°$ $c = 8.927(2)$ Å, $\gamma = 79.45(7)°$
V, Z	477.7(8) $Å^3$, 1
D(calcd)	3.19 Mg/m^3
abs coeff	15.290 mm^{-1}
F(000)	406
cryst size	0.02 × 0.03 × 0.09 mm
θ range for data collcn	2.68−32.23°
limiting indices	$0 \leq h \leq 9, -10 \leq k \leq 10, -12 \leq l \leq 12$
reflcns collcd	2990
indepdt reflcns	2781 [R(int) = 0.0346]
refinement method	full-matrix least-squares on F^2
data/restraints/params	2781/0/118
goodness-of-fit on F^2	0.935
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0363$, $wR2 = 0.0747$
R indices (all data)	$R1 = 0.0496$, $wR2 = 0.0777$
largest diff peak and hole	1.16 and −1.31e·$Å^{-3}$

Kα radiation. The unit cell dimensions were determined and refined using the positions of 46 high-angle reflections (20° < 2θ < 52°). The intensities of three standard reflections measured every 97 reflections showed no decay during data collection. The cell unit parameters and intensity data provided strong evidence for the centric space group $P\bar{1}$. The structure was successfully solved and refined in this space group. Lorentz, polarization, and background corrections were applied to the data using the Seimens P4 software.[12] The position of the W atom was solved by the Patterson method, and the remaining non-H atoms were located by successive difference Fourier syntheses. Non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques on F^2. The H-atom positions were calculated, and the atoms were constrained as riding atoms with U isotropic 20% larger than the corresponding C-atom. No secondary extinction correction was applied to the data. All calculations were performed using SHELXTL version 5 on a personal computer.[12]

Selected experimental details of the X-ray determination are given in Table 1, and final positional parameters are given in the Supporting Information. Anisotropic thermal parameters and hydrogen atom parameters are available as Supporting Information. Table 2 contains selected bond distances and angles. Figure 1 presents a molecular diagram of **1**.

Table 2. Bond Lengths [Å] and Angles [deg] for 1[a]

W−C(2)	1.992(9)	C(1)−O(1)	1.129(10)
W−C(1)	1.997(8)	C(2)−O(2)	1.157(10)
W−C(3)	2.019(9)	C(3)−O(3)	1.127(10)
W−C(5)	2.304(7)	C(4)−C(8)	1.417(10)
W−C(6)	2.324(8)	C(4)−C(5)	1.422(10)
W−C(4)	2.337(7)	C(4)−C(4′)	1.48(2)
W−C(7)	2.364(8)	C(5)−C(6)	1.443(11)
W−C(8)	2.375(7)	C(6)−C(7)	1.422(11)
W−I	2.852(3)	C(7)−C(8)	1.403(11)
C(2)−W−C(1)	76.5(3)	O(3)−C(3)−W	175.4(8)
C(2)−W−C(3)	112.5(4)	C(8)−C(4)−C(5)	107.7(7)
C(1)−W−C(3)	79.3(4)	C(8)−C(4)−C(4′)	126.0(9)
C(1)−W−I	133.6(2)	C(5)−C(4)−C(4′)	126.2(9)
C(2)−W−I	76.2(2)	C(4)−C(5)−C(6)	108.0(7)
C(3)−W−I	77.5(3)	C(7)−C(6)−C(5)	106.7(7)
O(1)−C(1)−W	178.0(7)	C(8)−C(7)−C(6)	108.9(7)
O(2)−C(2)−W	175.9(8)	C(7)−C(8)−C(4)	108.7(7)

[a] Symmetry transformations used to generate equivalent atoms: $-x + 1, -y + 1, -z$.

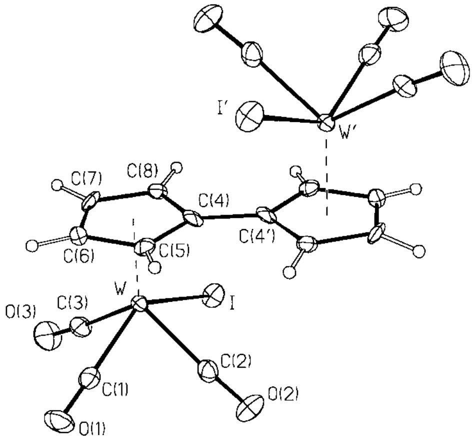
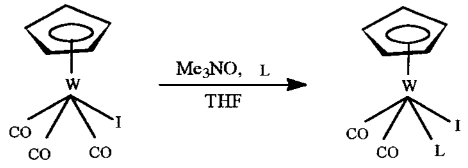


Figure 1. View of molecule **2** with 25% probability ellipsoids drawn for W, C, and O. For clarity, H atoms are represented as open spheres.

Results and Discussion

Phosphine Substitution Reactions of (η^5-C_5H_5)W(CO)$_3$I and (η^5:η^5-$C_{10}H_8$)W_2(CO)$_6I_2$. Phosphine-substituted cyclopentadienyltungsten carbonyl halo compounds (η^5-C_5H_5)W(CO)$_2$LI (**3**−**9**) (L = P(OMe)$_3$, PPhMe$_2$, P(n-Bu)$_3$, PPh$_2$Me, P(p-tol)$_3$, P(m-tol)$_3$, and PCy$_3$) were readily prepared by direct thermal substitution of a CO ligand in moderate yield (∼50%) using a modification of the traditional method.[7a] In these reactions the only product obtained was a covalent monosubstituted derivative, and neither disubstitution (η^5-C_5H_5)W(CO)L_2I nor ionic (η^5-C_5H_5)W(CO)$L_2^+I^-$ products were formed. All reactions were completed in ∼1−7 days on heating to 90 °C. During the course of these reactions we did not observe thermal decomposition of (η^5-C_5H_5)W(CO)$_3$I, in the presence of phosphine, to [(η^5-C_5H_5)W(CO)$_3$]$_2$. When these reactions were carried out in presence of 1 equiv of Me_3NO, they proceeded in predictable fashion to give only monosubstituted species as final product in high yield (∼93%) (eq 1). This new method for synthesis of organometallic complexes with P-donor ligands has clear advantages over the traditional method previously used, namely, mild conditions, short reaction times, higher yields, and no requirement of excess ligand. In order to compare the efficiency of this new procedure, we have gathered the yields and conditions of both methods in Table 3.



(1)

L= P(OMe)$_3$ (**3**), PPhMe$_2$ (**4**), P(n-Bu)$_3$ (**5**), PPh$_2$Me (**6**), P(p-tol)$_3$ (**7**), P(m-tol)$_3$ (**8**), PCy$_3$ (**9**) (95% yield)

Phosphine-substituted (fulvalene)dimolybdenum carbonyl dihalo compounds containing PPh$_3$, PCy$_3$, and PXy$_3$ are readily prepared, under thermal conditions, by direct substitution of a CO ligand at each Mo center

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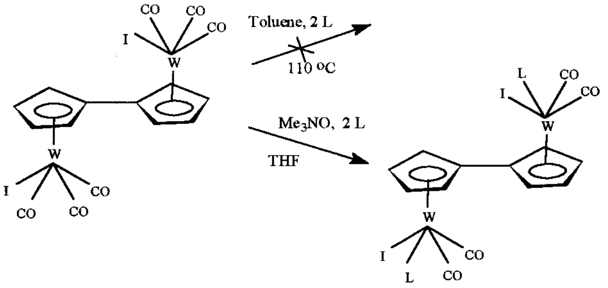
[12] Sheldrick, G.M. *SHELXTL/PC, Users Manual*, Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1990.

Table 3. Comparison of Me_3NO (A) and Direct Thermal (B) Substitution Methods in the $(\eta^5:\eta^5\text{-}C_{10}H_8)W_2(CO)_4L_2I_2$ Synthesis

compd	method	time	yield (%)
3	A	10 min	95
3	B	2 days	65
4	A	5 min	93
4	B	1 day	63
5	A	5 min	96
5	B	3 days	55
6	A	5 min	90
6	B	3 days	60
7	A	10 min	80
7	B	7 days	50
8	A	12 min	90
8	B	7 days	60
9	A	15 min	99
9	B	7 days	98

of the parent dihalides.[7b] These substitution reactions are facile and with bulky ligands possible to complete in ~10 min−2 h on heating to 110 °C. *Surprisingly,* contrary to what was expected, when we treated $(\eta^5:\eta^5\text{-}C_{10}H_8)W_2(CO)_6I_2$ with $PPhMe_2$, PPh_2Me, or PCy_3 under thermal conditions, no reaction was observed. Interestingly, while a considerable amount (<40%) of $(\eta^5:\eta^5\text{-}C_{10}H_8)Mo_2(CO)_6I_2$ decomposed to $(\eta^5:\eta^5\text{-}C_{10}H_8)Mo_2(CO)_6$ under thermal conditions in the presence of added phosphine,[7b] we have found that the analogous $(\eta^5:\eta^5\text{-}C_{10}H_8)W_2(CO)_6I_2$ does not decompose thermally in both THF at ~80 °C or toluene at ~110 °C for a period of 5 days. In order to obtain phosphine-substituted (fulvalene)ditungsten carbonyl dihalo we have used a new general procedure of synthesis using Me_3NO to remove one CO molecule at each metal center of the dihalide complexes. These reactions take place easily under mild conditions, and $(\eta^5:\eta^5\text{-}C_{10}H_8)W_2(CO)_4L_2I_2$ (**10**−**13**) (L = $P(OMe)_3$, $PPhMe_2$, PPh_2Me, and PCy_3) complexes were readily obtained by reaction of $(\eta^5:\eta^5\text{-}C_{10}H_8)W_2(CO)_6I_2$ with P-donor ligands in the presence of 2 equiv of trimethylamine *N*-oxide (eq 2).



(2)

L= $P(OMe)_3$ (**10**), $PPhMe_2$ (**11**), PPh_2Me (**12**), PCy_3 (**13**)

The complexes **3**−**9** and **10**−**13** were isolated as brown-reddish solids. They are very air sensitive. The fulvalene derivatives are very insoluble in hexane, toluene, or diethyl ether while the cyclopentadienyl ones exhibit a high solubility.

The IR spectra of these complexes exhibit two carbonyl stretching bands at ca. 1960 and 1850 cm^{-1} (see Experimental Section), characteristic of terminal carbonyl ligands. As expected, the ν_{CO} stretching frequencies depend on the nature of the substituents and become greater when the nucleophilic basicity of the P-donor ligands decreases.

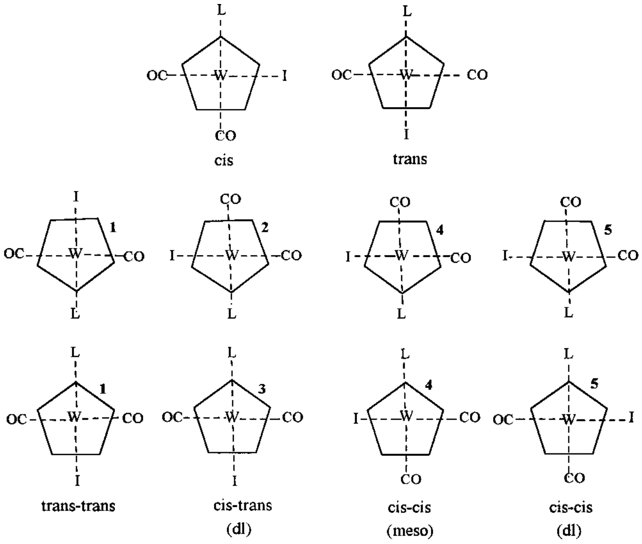


Figure 2. Schematic representation of the two and four different stereoisomers of $(\eta^5\text{-}C_5H_5)W(CO)_3LI$ and $(\eta^5:\eta^5\text{-}C_{10}H_8)W_2(CO)_4L_2I_2$, respectively.

The complexes $(\eta^5\text{-}C_5H_5)W(CO)_2LI$ may exist as a mixture of *cis* and *trans* isomers (Figure 2). The relative proportion of these isomers depends markedly on the nature of the phosphorus ligands and the method of preparation as well as the solvent.[13] The identity of the isomers was proven according to well-established infrared and NMR criteria.[13a,14] The higher frequency (symmetric) CO stretching vibration is more intense than the lower frequency (antisymmetric) stretch for the *cis* isomers, while the opposite is true for the *trans* isomers. When L = PCy_3,[11] $P(n\text{-}Bu)_3$, and PPh_2Me, the *cis* isomer is in high proportion, while for L = $P(OMe)_3$, $PPhMe_2$, $P(p\text{-}tol)_3$, and $P(m\text{-}tol)_3$ is the *trans* isomer. These isomers may be readily distinguished by the characteristic $(\eta^5\text{-}C_5H_5)$ resonances in the NMR spectrum. The ^1H NMR spectra show that the monosubstituted complexes exist as a mixture of two isomers; the resonances due to the $(\eta^5\text{-}C_5H_5)$ protons of *cis* isomers are found as a singlet at ca. 5.40 ppm, while those due to the *trans* isomers consist of a 1:1 doublet, at ca. 5.20 ppm (J_{PH} = 1.8 Hz), due to coupling with phosphorus (Experimental Section). The ratio of the isomers can be easily calculated from the integrals of these *cis* and *trans* resonances and is dependent on the electronic as well as the steric factors of the ligands. For the $P(OMe)_3$ and PCy_3 ligands the steric effects are predominant; thus, for the $P(OMe)_3$ ligand, with the smaller cone angle (θ = 107°),[15] the *trans* isomer is predominant, while for the PCy_3 ligand, with the greater cone angle (θ = 170°), the *cis* isomer is favored. For the rest of the ligands, $PPhMe_2$, $P(n\text{-}Bu)_3$, PPh_2Me, $P(p\text{-}tol)_3$, and $P(m\text{-}tol)_3$, the electronic effects are an important contributing factor in determining the equilibrium ratio of isomers, but they do not always dominate with regard to conformational preference. It thus appears that steric factors must also be responsible in large measure for the isomer ratios observed. The *cis* and

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[13] (a) Faller, J. W.; Anderson, A. S. *J. Am. Chem. Soc.* **1970**, *92*, 5852. (b) Beach, D. L.; Barnett, K. W. *J. Organomet. Chem.* **1975**, *97*, C27.

[14] (a) Manning, A. R. *J. Chem. Soc. A* **1967**, 984. (b) Beach, D. L.; Dattilo, M.; Barnett, K. W. *J. Organomet. Chem.* **1977**, *140*, 47.

[15] Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

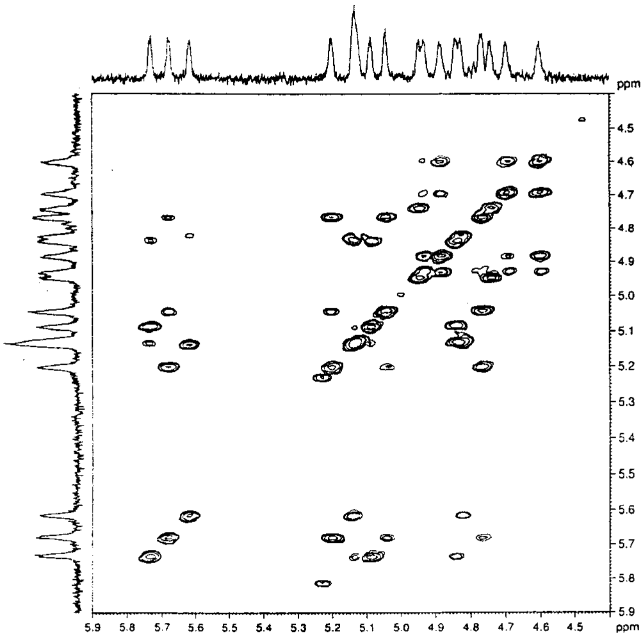

Figure 3. COSY experiment for **12** in $CDCl_3$.

trans isomers can be easily separated by TLC using DMC/hexane (1:2) as eluent. The complexes are stable with respect to isomerization both in the solid state and in solution at low temperature. However, when solutions of the pure *cis* and *trans* isomers in THF are heated to 70 °C, rapid isomerization occurs, while at 30 °C the isomerization proceeds more slowly. The ^{31}P NMR spectra at room temperature exhibit two singlets assigned to the *cis* and *trans* isomers (Experimental Section). The ratio of *cis*:*trans* isomers obtained from the integrals of these resonances agreed reasonably well with that obtained from ^1H NMR data.

The compounds $(\eta^5:\eta^5\text{-}C_{10}H_8)W_2(CO)_4L_2I_2$ may exist as four different geometrical isomers (not including enantiomers), *trans*−*trans*, *cis*−*trans* (*d,l*), *cis*−*cis* (*meso*), and *cis*−*cis* (*d,l*) (*cis*−*cis* isomers contain two chiral centers)[3] (Figure 2). The compounds have very similar infrared spectra in the 2100−1800 cm^{-1} region. When L = PPh_2Me and PCy_3, the more intense the two absorptions due to the two CO stretching vibrations, the higher the frequency (the intensity ratio is consistent with basically the *cis* geometry), while when L = $P(OMe)_3$ and $PPhMe_2$, the lower frequency gives rise to the more intense absorption in the IR spectrum (basically *trans* geometry). The ^1H NMR data for these complexes are listed in the Experimental Section. The spectra have been assigned on the basis of chemical shift, integrals, spin−spin coupling information, and two-dimensional homonuclear correlation spectroscopy (COSY and NOESY).[16] The ^1H NMR spectra can give rise to 18 signal due to fulvalene proton rings (nine α- and β-hydrogen sites). Since the substituted cyclopentadienylmolybdenum[13b] and -tungsten carbonyl halides and $(\eta^5:\eta^5\text{-}C_{10}H_8)Mo_2(CO)_4(PMe_3)_2H_2$[3] are fluxional, facile interconversion of the various *cis* and *trans* isomers of $(\eta^5:\eta^5\text{-}C_{10}H_8)W_2(CO)_4L_2I_2$ was also anticipated. For L = PPh_2Me (**12**) the ^1H NMR shows 14 signals in the range 5.80−4.58 ppm for the fulvalene resonances, 4 of them completely overlapping at 5.16, 4.95 and 4.89 ppm. Figure 3 shows the COSY spectrum of this complex, including the normal (1D) spectrum for comparison of the diagonal connectivities; the protons corresponding to each of the fulvalene rings (Figure 3) can be distinguished and assigned unambiguously (Experimental Section). The ratio of *trans*−*trans*, *cis*−*trans*, *cis*−*cis* (*meso*), and *cis*−*cis* (*dl*) was found to be 11:44:22:22 on the basis of integrals. ^{31}P NMR spectrum of **12** exhibits five resonances at δ 10.4 (*trans*), 10.1 (*cis*−*trans*), −4.4 and −4.5 (*cis*−*cis*), and −4.6 (*cis*−*trans*). The ^1H NMR spectrum of **13** shows 8 fulvalene signals corresponding to two different rings of two different fulvalene systems, *cis*−*cis* (*meso*) and *cis*−*cis* (*dl*) isomers, in which the halves are spectroscopically identical (Experimental Section). In agreement with this, the ^{31}P NMR spectrum of **13** exhibits only one singlet at 52.30 ppm. ^1H NMR spectra **10** and **11** exhibit 10 fulvalene signals corresponding to five different rings of the four isomers. In accordance with this, the ^{31}P NMR spectra exhibit four resonances at δ 146.7 (*trans*−*trans*), 145.5 (*cis*−*trans*), 133.2 (*cis*−*trans*), 134.8 (*cis*−*cis*) and 34.7 (*trans*−*trans*), 33.1 (*cis*−*trans*), 25.9 (*cis*−*trans*), and 24.5 (*cis*−*cis*), respectively. The isomer ratios of *trans*−*trans*, *cis*−*trans*, *cis*−*cis* (*meso*), and *cis*−*cis* (*dl*) for **10** and **11** were found to be 66:30:4:4 and 36:50:7:7, respectively, on the basis of integrals. The *cis*:*trans* ratios found for (fulvalene)ditungsten complexes are similar to that for cyclopentadienyltungsten analogous compounds.

Preliminary results carried out in our laboratory have revealed that the (fulvalene)dimolybdenums $(\eta^5:\eta^5\text{-}C_{10}H_8)Mo_2(CO)_6I_2$ and $(\eta^5:\eta^5\text{-}C_{10}H_8)Mo_2(CO)_6$ reacts with PCy_3 and PMe_3, respectively, in the presence of Me_3NO under mild conditons to give the disubstituted[17] and zwitterion[18] products, respectively. All these results show that this method is a very efficient and general way to obtain disubstituted fulvalene or cyclopentadienyl complexes.

Description of the Crystal and Molecular Structure of $(\eta^5:\eta^5\text{-}C_{10}H_8)W_2(CO)_6I_2$ (2). The crystal structure consists of one discrete molecule of **2** per unit cell. Complex **2** possesses a crystallographically imposed center of inversion. The two $W(CO)_3I$ units are on opposite sides of a fulvalene ligand as shown in Figure 1. The fulvalene ligand adopts the 1,1′-(η^5:η^5) binding mode, and the W centers have a four-legged piano stool structure (square pyramidal). The dihedral angle between the two Cp planes of the fulvalene ligand is 0° (symmetry imposed). In **2**, the C−C bridgehead distance, C(4)−C(4′) (1.48(2) Å), and the mean C=O bond length (1.138(18) Å) are normal.[19] The W−Cp ring carbon distances range from 2.304(7) to 2.375(7) Å; these values are consistent with W−Cp ring carbon distances seen in other compounds. The W−I distance, 2.852(3) Å, also is normal.[19]

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[16] (a) Kessler, H.; Gehrke, M.; Griesinger, C. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 490. (b) Martin, G. E.; Zektler, A. S. In *Two-Dimensional NMR Methods for Establishing Molecular Connectivity*; VCH: New York, 1988.

[17] Moreno, C.; Gomez-Escudero, J. L.; Marcos, M. L.; Macazaga, M. J.; Medina, R.; González-Velasco, J.; Delgado, S. Unpublished work.

[18] Moreno, C.; Marcos, M. L.; Macazaga, M. J.; Medina R. M.; Farrar, D. H.; González-Velasco, J.; Delgado, S. *Organometallics*, submitted for publication.

[19] Allen, F. H.; Kennard, O. *Chem. Des. Autom. News* **1993**, *8*, 31.

Acknowledgment. We express our great appreciation of the financial support from the DGICYT (Project PB 91-0003) of Spain. Acknowledgments are made (by D.H.F.) to the Natural Sciences and Engineering Research Council (NSERC) of Canada for equipment funds. Alan Lough is thanked for his technical assistance regarding the X-ray structure determination.

Supporting Information Available: Tables of X-ray data, complete positional and thermal parameters, and bond distances and angles (5 pages). Ordering information is given on any current masthead page.

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