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Insertions of Heterocumulenes into the M–C σ-Bonds of $Cp^*M(NO)(aryl)_2$ (M = Mo, W) Complexes[1]

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Summary: Treatment of the 16-valence-electron complexes $Cp^*M(NO)(aryl)_2$ ($Cp^* = \eta^5$-C_5Me_5; M = Mo, W; aryl = phenyl (Ph), p-tolyl) with the heterocumulenes carbon disulfide, p-tolyl isocyanate, and carbon dioxide leads to the η^2-thiocarboxylate, η^2-amide-, and η^2-carboxylate-containing complexes, respectively, in 10–65% isolated yields. Furthermore, $Cp^*W(NO)(\eta^2$-S_2C-$Ph)(Ph)$ (1) reacts with trimethylphosphine to form $Cp^*W(NO)(\eta^2$-$S_2C(PMe_3)Ph)(Ph)$ (10), which contains a zwitterionic phosphonium betaine ligand. The solid-state molecular structure of 10-CH_2Cl_2 has been established by a single-crystal X-ray crystallographic analysis. Crystal data for $Cp^*W(NO)(\eta^2$-$S_2C(PMe_3)Ph)(Ph)\cdot CH_2Cl_2$: monoclinic, a = 8.482(1) Å, b = 27.410(2) Å, c = 13.054(3) Å, β = 92.02(1)°, Z = 4, space group $P2_1/n$ (No. 14), R_F = 0.029, and R_{wF} = 0.027 for 5374 reflections with $I \geq 3\sigma(I)$.

In previous work we have established that the monomeric $Cp'M(NO)R_2$ systems ($Cp' = Cp$ (η^5-C_5H_5), Cp^* (η^5-C_5Me_5); M = Mo, W; R = alkyl, aryl) constitute a unique family of 16-valence-electron complexes possessing three-legged piano-stool molecular structures.[2] One type of reactivity that we have not previously explored with the $Cp'M(NO)R_2$ systems is their behavior of toward CO_2 and related heterocumulenes. Such studies of the reactivity of heterocumulenes with metal–aryl and metal–alkyl complexes have received increased attention in recent years for a variety of reasons.[3] In general, heterocumulenes have been found to be more reactive than CO_2 due primarily to their increased electrophilicities and bond polarities. In this note we briefly describe the insertion reactions of carbon dioxide, carbon disulfide, and p-tolyl isocyanate with the recently reported $Cp^*M(NO)(aryl)_2$ (M = Mo, W) complexes.[4]

Experimental Section

All reactions and subsequent manipulations involving organometallic reagents were performed under anaerobic and anhydrous conditions under an atmosphere of prepurified dinitrogen. Conventional drybox and vacuum-line Schlenk techniques were utilized throughout.[5,6] General procedures routinely employed in these laboratories have been described in detail previously.[4] All reagents were purchased from commercial suppliers or were prepared according to literature methods. Thus, $Cp^*M(NO)(aryl)_2$[4] (M = Mo, W; aryl = Ph, p-tolyl) and diphenylketene[7] were synthesized by the published procedures. CS_2 (99+%, Aldrich) was distilled from P_2O_5, while CO_2 (99.999%, Matheson) and CO (Linde/Union Carbide) were used as received.

General Synthetic Procedures Employed during This Study. All solid reagents such as $Cp^*W(NO)(aryl)_2$ were weighed in a glovebox into a glass bomb equipped with a 4-mm Teflon stopcock. The flask was removed from the box, and subsequent manipulations were performed on a vacuum line. Unless indicated otherwise, solvents were added via vacuum transfer to the reaction vessel at −196 °C. Isolated yields for all products are listed in Table I, and the spectroscopic and physical properties of all complexes are collected in Tables I–III.

Preparation of $Cp^*W(NO)(\eta^2$-S_2C-aryl)(aryl) (Aryl = Ph (1), p-Tolyl (2)) and $Cp^*Mo(NO)(\eta^2$-S_2C-p-tolyl)(p-tolyl) (3). The syntheses of these complexes were quite similar, and the preparation of complex 1 is described as a representative example. In a glass bomb were placed benzene (5 mL), excess CS_2 (0.2 mL), and $Cp^*W(NO)Ph_2$ (0.27 g, 0.54 mmol). The solution was freeze–pump–thaw-degassed twice and was left under partial vacuum. Stirring of the solution at room temperature for 2 days was accomplished by a change in color from blue to purple. The solvent was removed in vacuo, and the residue was dissolved in Et_2O (20 mL). Chromatography of the purple extracts on a column of neutral alumina I (3 × 8 cm) provided a purple eluate, which was reduced in volume until crystallization was initiated. Cooling of this mixture overnight at −30 °C resulted in the deposition of a purple microcrystalline solid. Similar procedures led to the isolation of complexes 2 and 3 from CH_2Cl_2 at −30 °C.

Preparation of $Cp^*W(NO)(\eta^2$-N(p-tolyl)C(O)aryl)(aryl) (Aryl = Ph (4), p-Tolyl (5)) and $Cp^*Mo(NO)(\eta^2$-N(p-tolyl)C(O)-p-tolyl)(p-tolyl) (6). The syntheses of these complexes were quite similar, and therefore they are described in a general manner. Benzene (10 mL) was added to $Cp^*M(NO)(aryl)_2$ (0.50 mmol), and to this stirred solution was added excess p-tolyl isocyanate (0.20 mL, 1.5 mmol). The resulting solution was freeze–pump–thaw-degassed twice and left under partial vacuum. Over the course of 3 days at ambient temperatures, the stirred solutions changed from purple (M = Mo) or blue (M = W) to yellow-brown. The solvent was removed from the final solution in vacuo, and the remaining oily brown residue was triturated with cold pentane (10 mL). The resulting residue was dissolved in Et_2O and filtered through Celite (2 × 3 cm) supported on a medium-porosity frit. Pentane (10 mL) was added to the filtrate, and crystallization of the desired product was effected over 1 week at −30 °C.

Preparation of $Cp^*W(NO)(\eta^2$-$O_2CPh)(Ph)$ (7). In a glass bomb were placed benzene (15 mL) and $Cp^*W(NO)Ph_2$ (0.84 g, 2.0 mmol). The blue solution was freeze–pump–thaw-degassed three times, and the vessel was then pressurized with CO_2 (1–2 atm). Heating the solution at 60 °C for 3 days led to a change in color to amber-brown. The benzene solution was transferred via cannula to a Schlenk tube, and the solvent was removed in vacuo. The brown residue was dissolved in Et_2O (20 mL), and

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(1) (a) Taken in part from: Brouwer, E. B. M.Sc. Dissertation, The University of British Columbia, 1992. (b) Presented in part at the 75th Canadian Chemical Conference, Edmonton, Alberta, Canada, June 1992; Abstract 395.

(2) Legzdins, P.; Veltheer, J. E. *Acc. Chem. Res.* **1993,** *26,* 41.

(3) For a recent example, see: Vivanco, M.; Ruiz, J.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1993,** *12,* 1794.

(4) Dryden, N. H.; Legzdins, P.; Rettig, S. J.; Veltheer, J. E. *Organometallics* **1992,** *11,* 2583.

(5) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds,* 2nd ed.; Wiley-Interscience: Toronto, 1986.

(6) Wayda, A. L.; Darensbourg, M. Y. *Experimental Organometallic Chemistry: A Practicum in Synthesis and Characterization;* ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987.

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Table I. Numbering Scheme, Color, Yield, and Elemental Analysis Data for Complexes 1–10

complex	compd no.	color (% yield)	anal. found (calcd) C	H	N
$Cp^*W(NO)(\eta^2\text{-}S_2CPh)(Ph)$	1	purple (54)	47.87 (47.67)	4.32 (4.35)	2.41 (2.42)
$Cp^*W(NO)(\eta^2\text{-}S_2C\text{-}p\text{-tolyl})(p\text{-tolyl})$	2	purple (48)	49.47 (49.43)	4.81 (4.86)	2.18 (2.30)
$Cp^*Mo(NO)(\eta^2\text{-}S_2C\text{-}p\text{-tolyl})(p\text{-tolyl})$	3	red (44)	57.58 (57.79)	5.77 (5.62)	2.53 (2.70)
$Cp^*W(NO)(\eta^2\text{-}N(p\text{-tolyl})C(O)Ph)(Ph)$	4	orange (42)	56.41 (56.62)	5.10 (5.07)	4.47 (4.40)
$Cp^*W(NO)(\eta^2\text{-}N(p\text{-tolyl})C(O)\text{-}p\text{-tolyl})(p\text{-tolyl})$	5	yellow (65)	57.50 (57.84)	5.63 (5.46)	3.99 (4.22)
$Cp^*Mo(NO)(\eta^2\text{-}N(p\text{-tolyl})C(O)\text{-}p\text{-tolyl})(p\text{-tolyl})$	6	yellow (43)	66.42 (66.66)	6.31 (6.29)	4.89 (4.86)
$Cp^*W(NO)(\eta^2\text{-}O_2CPh)(Ph)$	7	yellow (10)	51.35 (50.48)	4.97 (4.60)	2.53 (2.56)
$Cp^*W(NO)(\eta^2\text{-}O_2CPh)(Cl)$	8	orange (73)	39.99 (40.38)	4.03 (3.99)	2.66 (2.77)
$Cp^*W(NO)(\eta^2\text{-}O_2CCD_3)(Ph)$	9	yellow[a]			
$Cp^*W(NO)(\eta^2\text{-}S_2C(PMe_3)Ph)(Ph)$	10	gold (61)	48.02 (47.64)	5.31 (5.23)	2.00 (2.14)

[a] The yield was quantitative by ^{1}H NMR spectroscopy.

Table II. Mass Spectral and Infrared Data for Complexes 1–10

compd no.	MS, m/z[a]	probe temp, °C	IR (Nujol), cm^{-1}
1	579 [P]$^+$, 549 [P − NO]$^+$	150	1578 (ν_{NO}); 1176 (ν_{CS_2}); 1005 (ν_{CS_2})
2	607 [P]$^+$	80	1580 (ν_{NO}); 1174 (ν_{CS_2}); 1021 (ν_{CS_2})
3	521 [P]$^+$, 491 [P − NO]$^+$	120	1597 (ν_{NO}); 1175 (ν_{CS_2}); 1020 (ν_{CS_2})
4	636 [P]$^+$, 606 [P − NO]$^+$	150	1601 (ν_{CN}); 1576 (ν_{NO}); 1397 (ν_{CO})
5	664 [P]$^+$	120	1603 (ν_{CN}); 1561 (ν_{NO}); 1392 (ν_{CO})
6	578 [P]$^+$	150	1609 (ν_{CN}); 1584 (ν_{NO}); 1418 (ν_{CO})
7	503 [P − CO$_2$]$^+$	120	1585 (ν_{NO}); 1480 (ν_{CO_2}); 1362 (ν_{CO_2})
8	505 [P]$^+$, 475 [P − NO]$^+$	180	1597 (ν_{NO}); 1508 (ν_{CO_2}); 1457 (ν_{CO_2})
9	518 [P]$^+$	80	1584 (ν_{NO}); 1485 (ν_{CO_2}); 1393 (ν_{CO_2})
10	579 [P − PMe$_3$]$^+$	80	1548 (ν_{NO})

[a] The m/z values are for the highst intensity peak of the calculated isotopic cluster, i.e., ^{98}Mo and ^{184}W.

the extracts were chromatographed on a column of neutral alumina I (3 × 8 cm). An orange-brown band was eluted with THF (50 mL). The eluate was evaporated, and the residue was triturated with pentane. The resulting yellow powder was dissolved in a minimum of Et_2O and maintained at −30 °C for 6 days to induce the deposition of complex 7.

Preparation of $Cp^*W(NO)(\eta^2\text{-}O_2CPh)(Cl)$ (8). Solid $Cp^*W(NO)Cl_2$ (0.42 g, 1.0 mmol) and sodium benzoate (0.14 g, 1.0 mmol) were weighed in air and transferred to a Schlenk tube. The tube was evacuated and then cooled to −50 °C with a liquid nitrogen/actone bath. CH_2Cl_2 (30 mL) was added to the reaction flask, the bath removed, and the solution stirred overnight at room temperature. The color of the solution changed from green to yellow-brown during this time. The solvent was removed from the final mixture in vacuo, and the resulting brown residue was triturated with pentane (2 × 5 mL). This procedure afforded a yellow powder, which was dissolved in CH_2Cl_2 (20 mL) and filtered through a column of Celite (3 × 3 cm) supported on a sintered-glass frit. The orange filtrate was reduced in volume, and hexanes (5 mL) was added. Orange crystals of 8 formed upon maintaining this mixture overnight at −30 °C.

Treatment of $Cp^*W(NO)Ph_2$ and $Cp^*W(NO)(p\text{-tolyl})_2$ with Diphenylketene. THF (10 mL) was added to $Cp^*W(NO)Ph_2$ (0.36 g, 0.72 mmol), and an excess of diphenylketene (0.75 mL, 4.3 mmol) was added by pipet. The solution was freeze–pump–thaw-degassed twice and left under partial vacuum. Heating of the mixture at 65 °C for 16 h resulted in the formation of a brown solution, which was cooled and transferred to a Schlenk tube via cannula. The THF was removed under reduced pressure, and the residue was dissolved in Et_2O (20 mL). Chromatography was Et_2O as eluant on a column of neutral alumina (3 × 8 cm) led to the elution of two bands: the first, amber in color, was collected and upon removal of solvent afforded an intractable brown oil. The yellow second fraction was taken to dryness in vacuo, and crystallization of the residue from Et_2O at −30 °C afforded white crystals of diphenylmethyl phenyl ketone. Similarly, the reaction of $Cp^*W(NO)(p\text{-tolyl})_2$ with diphenylketene led to the isolation of diphenylmetyl p-tolyl ketone.

Reaction of $Cp^*W(NO)(\eta^2\text{-}N(p\text{-tolyl})C(O)Ph)(Ph)$ (4) with H_2O. Compound 4 (0.11 g, 0.17 mmol) was weighed out in air, transferred to a Schlenk tube, and placed under vacuum for 15 min, after which time Et_2O (15 mL) was added to obtain a yellow solution. Distilled water (0.5 mL, excess) was degassed for 5 min and was then added to the Et_2O solution. The reaction mixture was stirred at ambient temperature overnight. The solvent was removed from the final mixture, and the residue was sublimed onto a water-cooled probe under static vacuum at 100 °C for 1 day to obtain p-tolylbenzamide (0.025 g, 0.12 mmol, 71% yield) as a white microcrystalline solid.[8] The unsublimed residue was shown to contain $Cp^*W(O)_2Ph$ by IR spectroscopy and mass spectrometry.[9]

Reaction of $Cp^*W(NO)(\eta^2\text{-}N(p\text{-tolyl})C(O)Ph)(Ph)$ (4) with CD_3CO_2D. Complex 4 (0.035 g, 0.055 mmol) was dissolved in C_6D_6 (0.6 mL) in an NMR tube equipped with a Teflon stopcock, and an excess of acetic acid-d_4 (0.05 mL, 0.6 mL) was added. The yellow contents of the NMR tube were freeze–pump–thaw-degassed three times. ^{1}H NMR spectroscopy established that the products $Cp^*W(NO)(\eta^2\text{-}O_2CCD_3)(Ph)$ (9) and p-tolylbenzamide-d_1 had been formed quantitatively after 1 day at room temperature.

Reaction of $Cp^*W(NO)(\eta^2\text{-}N(p\text{-tolyl})C(O)Ph)(Ph)$ (4) with HCl. Complex 4 (0.11 g, 0.17 mmol) was weighed out in air, transferred to a Schlenk tube, and placed under vacuum for 15 min. THF (20 mL) was then added by vacuum transfer, and the reaction mixture was warmed to −20 °C to obtain an orange solution. A solution of HCl in Et_2O (0.22 M, 0.75 mL, 1.0 equiv of HCl) was added by syringe, and the progress of the reaction was monitored by solution IR spectroscopy in the ν_{NO} region of 1700–1550 cm^{-1}. After 1 h, the color of the solution had changed to lime green, and the IR spectrum indicated (a) the decrease of the ν_{NO} band at 1582 cm^{-1}, attributable to 4, to half of its original intensity and (b) the appearance of two new absorbances at 1678 and 1628 cm^{-1}. An additional aliquot of HCl/Et_2O (0.75 mL, 1.0 equiv of HCl) was then added. After 30 min, the solution had turned an intense green, and the IR spectrum exhibited only the signals at 1678 and 1628 cm^{-1} due to ν_{CO} of p-tolylbenzamide and ν_{NO} of $Cp^*W(NO)Cl_2$, respectively. The solvent was then removed under reduced pressure, and the resulting brown residue was identified by ^{1}H NMR spectroscopy and mass spectrometry as a mixture of $Cp^*W(NO)Cl_2$ and p-tolylbenzamide.

Synthesis of $Cp^*W(NO)(\eta^2\text{-}S_2C(PMe_3)Ph)(Ph)$ (10). A sample of $Cp^*W(NO)(\eta^2\text{-}S_2CPh)(Ph)$ (1; 0.115 g, 0.199 mmol)

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[8] p-Tolylbenzamide: IR (Nujol mull) ν_{CO} 1649 cm^{-1}; ^{1}H NMR (C_6D_6) δ 7.18–7.12 (m, 4H, Ar H), 6.85 (br s, 1H, NH), 6.70–6.53 (m, 5H, Ar H), 1.67 (s, 3H, Ar CH_3); ^{13}C{^{1}H} NMR (C_6D_6) δ 174.5 (C=O), 136.8, 136.3, 133.8, 131.4, 129.7, 127.5, 120.6 (C_{arom}), 20.8 (Ar CH_3); low-resolution mass spectrum (probe temperature 80 °C) m/z 211 ([P]$^+$).

[9] Legzdins, P.; Lundmark, P. J.; Phillips, E. C.; Rettig, S. J.; Veltheer, J. E. *Organometallics* **1992**, *11*, 2991.

Table III. ^{1}H and ^{13}C{^{1}H} NMR Data for Complexes 1–10

compd no.	^{1}H NMR (C_6D_6), δ^a	^{13}C{^{1}H} NMR (C_6D_6), δ^a
1	8.06 (d, *J* = 7.5, 2H, *o* Ar *H*), 8.02 (d, *J* = 8.4, 2H, *o* Ar *H*), 7.34 (t, *J* = 7.8, 2H, *m* Ar *H*), 7.18 (t, *J* = 7.4, 1H, *p* Ar *H*), 7.08 (t, *J* = 7.5, 1H, *p* Ar *H*), 6.90 (t, *J* = 7.6 Hz, 2H, *m* Ar *H*), 1.55 (s, 15H, $C_5(CH_3)_5$)	236.78 (S_2C), 169.40, 156.75 (C_{ipso}), 145.01, 139.64, 133.65, 128.60, 125.32, 123.68 (C_{arom}), 109.92 ($C_5(CH_3)_5$), 9.62 ($C_5(CH_3)_5$)
2	8.05 (d, *J* = 8.1, 2H, *o* Ar *H*), 7.80 (d, *J* = 7.8, 2H, *o* Ar *H*), 7.14 (d, *J* = 7.8, 2H, *m* Ar *H*), 6.98 (d, *J* = 8.4, 2H, *m* Ar *H*), 2.33 (s, 3H, Ar CH_3), 2.11 (s, 3H, Ar CH_3), 1.73 (s, 15H, $C_5(CH_3)_5$)	236.28 (S_2C), 165.33, 144.89 (C_{ipso}), 142.98, 139.44, 134.04, 129.52, 129.15, 123.91 (C_{arom}), 109.76 ($C_5(CH_3)_5$), 21.86, 21.61 (Ar CH_3), 9.82 ($C_5(CH_3)_5$)
3^b	8.23 (d, *J* = 8.4, 2H, *o* Ar *H*), 8.00 (d, *J* = 7.8, 2H, *o* Ar *H*), 7.27 (d, *J* = 8.1, 2H, *m* Ar *H*), 6.82 (d, *J* = 8.1, 2H, *m* Ar *H*), 2.32 (s, 3H, Ar CH_3), 1.94 (s, 3H, Ar CH_3), 1.61 (s, 15H, $C_5(CH_3)_5$)	144.89, 138.76 (C_{ipso}), 129.40, 128.78, 124.45 (C_{arom}), 111.65 ($C_5(CH_3)_5$), 21.44, 21.30 (Ar CH_3), 9.85 ($C_5(CH_3)_5$)
4	8.30 (d, *J* = 7.8, 2H, *o* Ar *H*), 7.43 (d, *J* = 7.5, 2H, *m* Ar *H*), 7.35 (d, *J* = 7.8, 2H, *o* Ar *H*), 7.23 (m, 3H, Ar *H*), 6.94–6.76 (m, 5H, Ar *H*), 2.02 (s, 3H, Ar CH_3), 1.56 (s, 15H, $C_5(CH_3)_5$)	176.06, 172.11 (C_{ipso}), 141.08, 137.42, 135.06, 133.38, 130.92, 129.94, 128.94, 128.17, 125.83, 125.51 (C_{arom}), 111.25 ($C_5(CH_3)_5$), 20.81 (Ar CH_3), 9.41 ($C_5(CH_3)_5$)
5^c	7.84 (d, *J* = 7.8, 2H, Ar *H*), 7.44 (d, *J* = 8.2, 2H, Ar *H*), 7.24 (s, 4H, Ar *H*), 7.22 (d, *J* = 7.8, 2H, Ar *H*), 7.23 (d, *J* = 8.2, 2H, Ar *H*), 7.16 (d, *J* = 8.2, 2H, Ar *H*), 2.48 (s, 3H, Ar CH_3), 2.43 (s, 3H, Ar CH_3), 2.41 (s, 3H, Ar CH_3), 1.87 (s, 15H, $C_5(CH_3)_5$)	171.58 (NCO), 141.43, 140.27, 136.60 (br), 134.92, 134.36, 130.06, 129.59, 129.26, 128.70, 128.53, 125.40 (C_{arom}), 111.92 ($C_5(CH_3)_5$), 21.55, 21.30, 21.01 (Ar CH_3), 9.53 ($C_5(CH_3)_5$)
6^c	7.62 (d, *J* = 8.1, 2H, *o* Ar *H*), 7.27 (d, *J* = 8.2, 2H, *o* Ar *H*), 7.06 (m, 4H, Ar *H*), 7.02 (m, 4H, Ar *H*), 2.33 (s, 3H, Ar CH_3), 2.29 (s, 3H, Ar CH_3), 2.28 (s, 3H, Ar CH_3), 2.02 (s, 3H, Ar CH_3), 1.56 (s, 15H, $C_5(CH_3)_5$)	173.29 (NCO), 141.46, 140.79, 135.33 (br), 129.83, 129.49, 129.30, 128.80, 128.48, 128.37, 127.28, 125.83 (C_{arom}), 112.98 ($C_5(CH_3)_5$), 21.48, 21.17, 20.97 (Ar CH_3), 9.58 ($C_5(CH_3)_5$)
7	7.65 (d, *J* = 6.6, 2H, *o* Ar *H*), 7.16 (d, *J* = 7.5, 2H, *m* Ar *H*), 7.08 (t, *J* = 7.8, 2H, *m* Ar *H*), 7.05 (t, *J* = 7.8, 1H, *p* Ar *H*), 6.93 (d, *J* = 8.4, 2H, *o* Ar *H*), 6.76 (t, *J* = 6.9, 1H, *p* Ar *H*), 1.72 (s, 15H, $C_5(CH_3)_5$)	158.29 (O_2C), 156.87, 142.14, 128.51, 126.83, 123.65, 122.85 (C_{arom}), 117.08 ($C_5(CH_3)_5$), 10.80 ($C_5(CH_3)_5$)
8	7.90 (d, *J* = 8.1, 2H, *o* Ar *H*), 7.03 (d, *J* = 7.8, 1H, *p* Ar *H*), 6.90 (t, *J* = 7.5, 2H, *m* Ar *H*), 1.72 (s, 15H, $C_5(CH_3)_5$)	180.41 (O_2C), 134.15, 129.19, 128.52 (C_{arom}), 115.38 ($C_5(CH_3)_5$), 9.41 ($C_5(CH_3)_5$)
9	7.90 (d, *J* = 7.2, 2H, *o* Ar *H*), 7.33 (d, *J* = 7.6, 2H, *m* Ar *H*), 7.17 (t, *J* = 7.8, 1H, *p* Ar *H*), 1.51 (s, 15H, $C_5(CH_3)_5$)	177.74 (O_2C), 135.60, 128.62, 125.90 (C_{arom}), 112.35 ($C_5(CH_3)_5$), 19.49 (m, CD_3), 9.10 ($C_5(CH_3)_5$)
10^{d,e}	8.20 (br s, 2H, *o* Ar *H*), 7.84 (d, *J* = 8.4, 2H, *o* Ar *H*), 7.34 (t, *J* = 7.2, 2H, *m* Ar *H*), 7.16 (t, *J* = 7.2, 1H, *p* Ar *H*), 7.14 (t, *J* = 7.2, 2H, *m* Ar *H*), 6.99 (t, *J* = 7.2, 1H, *p* Ar *H*), 1.70 (s, 15H, $C_5(CH_3)_5$), 0.86 (d, *J* = 12.6, 9H, $P(CH_3)_3$)	173.99, 138.49, 128.33, 128.27, 127.68, 127.56, 127.52, 123.84 (C_{arom}), 110.68 ($C_5(CH_3)_5$), 56.32 (d, J_{PC} = 54, S_2C), 10.14 ($C_5(CH_3)_5$), 7.20 (d, J_{PC} = 57, $P(CH_3)_3$)

^{a} Coupling constants in Hz. ^{b} Major and minor products observed, aryl proton and ^{13}C signals unresolved. ^{c} In $CDCl_3$; less than expected number of signals due to the effects of hindered rotation. ^{d} In CD_2Cl_2. ^{e} ^{31}P NMR: δ 28.17 (s).

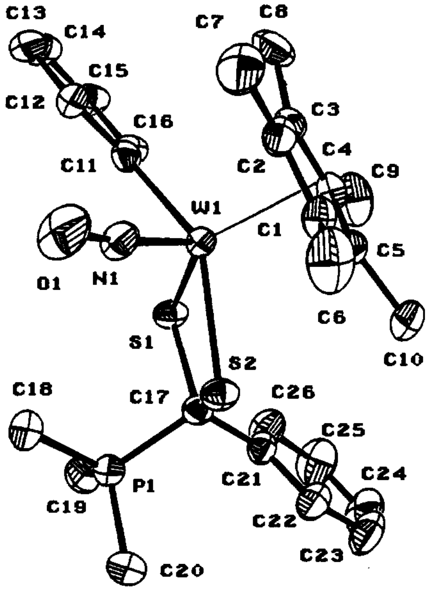

Figure 1. View of the solid-state molecular structure of $Cp^*W(NO)(\eta^2\text{-}S_2C(PMe_3)Ph)(Ph)\cdot CH_2Cl_2$ (**10**·CH_2Cl_2). Probability ellipsoids at the 33% level are shown for the non-hydrogen atoms, and the CH_2Cl_2 molecule of solvation has been omitted for clarity.

was dissolved in Et_2O (15 mL) in a Schlenk tube, and the solution was cooled to −196 °C. An excess of PMe_3 was vacuum-transferred into the Schlenk tube, and the contents were warmed to room temperature. A yellow-orange precipitate formed from the dark purple-red solution within minutes of thawing. After 30 min, the mixture was taken to dryness in vacuo, and the peach-colored powder was triturated with pentane (3 × 5 mL). The powder was recrystallized from CH_2Cl_2/hexanes at −30 °C over the course of 2 weeks to obtain analytically pure $Cp^*W(NO)(\eta^2\text{-}S_2C(PMe_3)Ph)(Ph)$ (**10**) as a golden solid.

X-ray Crystallographic Analysis of $Cp^*W(NO)(\eta^2\text{-}S_2C(PMe_3)Ph)(Ph)\cdot CH_2Cl_2$ (10·CH_2Cl_2). A prismatic orange crystal of **10**·CH_2Cl_2 was mounted in a thin-walled glass capillary and transferred to a Rigaku AFC6S diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda_{K\alpha}$ = 0.710 69 Å). Final unit-cell parameters for the complex were obtained by least-squares analysis of setting angles for 25 carefully centered reflections; $35.0 \leq 2\theta \leq 40.0°$. The intensities of three standard reflections were measured every 200 reflections during the data collection. These intensities showed linear 18% decreases with time, and so a linear correction factor was applied to the data to account for this phenomenon. The data were corrected for Lorentz and polarization effects and for absorption using the azimuthal scan method.[10] Pertinent crystallographic and experimental parameters for the complex are summarized in Table IV.

Interpretation of the Patterson function yielded the coordinates of the heaviest atoms in the structure, and the full structure of the compound was then derived by conventional electron density methods and was refined by full-matrix least-squares methods on *F*, minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o)^2$. Hydrogen atoms were fixed in calculated positions

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(10) TEXSAN/TEXRAY structure analysis package, which includes versions of the following: MITHRIL, integrated direct methods, by C. J. Gilmore; DIRDIF, direct methods for difference structures, by P. T. Beurskens; ORFLS, full-matrix least-squares, and ORFFE, functions and errors, by W. R. Busing, K. O. Martin, and H. A. Levy; ORTEP II, illustrations, by C. K. Johnson.

Table IV. Crystallographic Data for $Cp^*W(NO)(\eta^2\text{-}S_2C(PMe_3)Ph)(Ph)\cdot CH_2Cl_2$ ($\mathbf{10}\cdot CH_2Cl_2$)[a]

compd	**10**·CH_2Cl_2
formula	$C_{26}H_{34}NOPS_2W\cdot CH_2Cl_2$
fw	740.44
color, habit	orange, prism
cryst size, mm	0.30 × 0.40 × 0.45
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	8.482(1)
b, Å	27.410(2)
c, Å	13.054(3)
β, deg	92.02(1)
V, Å^3	3033(1)
Z	4
ρ_{calc}, g/cm^3	1.621
$F(000)$	1472
μ(Mo Kα), cm^{-1}	42.7
transmissn factors (relative)	0.60–1.00
scan type	ω
scan range, deg (in ω)	$0.91 + 0.35 \tan\theta$
scan rate, deg/min	32
data collected	$+h,+k,\pm 1l$
$2\theta_{max}$, deg	60
cryst decay, %	18.0
total no. of rflns	9580
no. of unique rflns	8837
R_{merge}	0.032
no. of rflns with $I \geq 3\sigma(I)$	5375
no. of variables	317
R	0.029
R_w	0.027
GOF	1.70
max Δ/σ (final cycle)	0.21
residual density, e/Å^3	–0.78 to +0.66 (near W)

[a] Conditions and collection details: temperature 294 K; Rigaku AFC6S diffractometer; Mo Kα radiation (λ = 0.710 69 Å); graphite monochromator; takeoff angle 6.0°; aperture 6.0 × 6.0 mm at a distance of 285 nm from the crystal; stationary background counts at each end of the scan (scan/background time ratio 2:1, up to 8 rescans); $\sigma^2(F^2) = [S^2(C + 4B)]/(L_p)^2$ (S = scan rate, C = scan count, B = normalized background count); function minimized $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$, $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$, and GOF $= [\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$. Values given for R, R_w, and GOF are based on those reflections with $I \geq 3\sigma(I)$.

with C–H = 0.98 Å and $U_H = 1.2U_{\text{bonded atom}}$. Non-hydrogen atoms were refined with anisotropic thermal parameters. A correction for secondary extinction was applied, the final value of the extinction coefficient being 1.48(6) × 10^{-7}. Complex neutral atom scattering factors (for all atoms) and anomalous scattering corrections for the non-hydrogen atoms were taken from ref 11. Final positional and equivalent isotropic thermal parameters for the complex are given in Table V, and selected bond lengths (Å) and bond angles (deg) are listed in Table VI. A view of the solid-state molecular structure of the complex **10**·CH_2Cl_2 is displayed in Figure 1.

Results and Discussion

Synthesis of the Inserted Complexes 1–8. Treatment of $Cp^*W(NO)Ph_2$ and $Cp^*M(NO)(p\text{-tolyl})_2$ (M = W, Mo) with the heterocumulenes CS_2, p-tolylNCO, and CO_2 leads to the η^2-thiocarboxylate-, η^2-amide-, and η^2-carboxylate-containing complexes, respectively, in 10–65% isolated yields as thermally robust and air-stable solids (eq 1). The benzoate chloride $Cp^*W(NO)(\eta^2\text{-}O_2CPh)$ (**8**), which is analogous to complex **7**, is obtainable by metathesis of $Cp^*W(NO)Cl_2$ with 1 equiv of sodium benzoate. However, treatment of complex **8** with various sources of 1 equiv of Ph^- does not produce **7** but, rather, results in decomposition.

Table V. Final Positional and Equivalent Isotropic Thermal Parameters (Å^2) for $Cp^*W(NO)(\eta^2\text{-}S_2C(PMe_3)Ph)(Ph)\cdot CH_2Cl_2$ ($\mathbf{10}\cdot CH_2Cl_2$)[a]

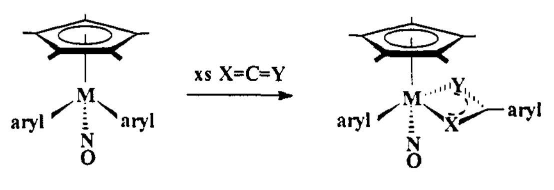
atom	x	y	z	B_{eq}
W(1)	0.30894(2)	0.350948(6)	0.42478(1)	2.856(7)
S(1)	0.2788(1)	0.41378(4)	0.5608(1)	3.73(5)
S(2)	0.5128(1)	0.33854(4)	0.5656(1)	3.84(5)
P(1)	0.5900(1)	0.43279(4)	0.6571(1)	4.00(6)
O(1)	0.5589(5)	0.3629(2)	0.2730(3)	8.4(3)
N(1)	0.4607(4)	0.3606(1)	0.3394(3)	4.6(2)
C(1)	0.2955(5)	0.2675(2)	0.4071(4)	4.1(2)
C(2)	0.2073(7)	0.2881(2)	0.3238(4)	4.4(2)
C(3)	0.0713(6)	0.3099(2)	0.3645(4)	4.2(2)
C(4)	0.0772(5)	0.3030(2)	0.4712(4)	3.8(2)
C(5)	0.2101(6)	0.2760(2)	0.4981(4)	3.8(2)
C(6)	0.4433(7)	0.2374(2)	0.3970(6)	7.6(4)
C(7)	0.2404(9)	0.2830(2)	0.2124(4)	7.6(4)
C(8)	–0.0684(7)	0.3290(2)	0.3033(6)	7.5(4)
C(9)	–0.0466(7)	0.3190(2)	0.5451(6)	7.2(4)
C(10)	0.2478(7)	0.2551(2)	0.6026(4)	6.1(3)
C(11)	0.1770(5)	0.4085(1)	0.3402(4)	3.5(2)
C(12)	0.2029(6)	0.4165(2)	0.2363(4)	4.3(2)
C(13)	0.1188(7)	0.4513(2)	0.1779(4)	5.7(3)
C(14)	0.0063(7)	0.4789(2)	0.2230(5)	6.3(3)
C(15)	–0.0239(7)	0.4732(2)	0.3236(5)	5.7(3)
C(16)	0.0586(6)	0.4383(2)	0.3809(4)	4.5(2)
C(17)	0.4342(5)	0.3872(1)	0.6445(3)	3.4(2)
C(18)	0.6617(6)	0.4497(2)	0.5354(4)	5.4(3)
C(19)	0.5200(7)	0.4857(2)	0.7193(4)	5.6(3)
C(20)	0.7526(6)	0.4094(2)	0.7317(4)	5.6(3)
C(21)	0.3814(6)	0.3720(2)	0.7504(3)	3.8(2)
C(22)	0.4530(7)	0.3343(2)	0.8041(4)	5.2(3)
C(23)	0.406(1)	0.3218(2)	0.9013(5)	7.1(4)
C(24)	0.290(1)	0.3476(3)	0.9450(5)	8.3(5)
C(25)	0.2155(9)	0.3851(3)	0.8938(5)	7.8(4)
C(26)	0.2595(7)	0.3973(2)	0.7965(4)	5.7(3)
Cl(1)	0.3221(3)	0.12491(8)	0.5180(2)	10.6(1)
Cl(2)	0.1542(4)	0.0372(1)	0.5262(2)	16.4(2)
C(27)	0.1941(9)	0.0907(3)	0.5856(6)	8.9(5)

[a] $B_{eq} = {}^8/_3\pi^2\sum\sum U_{ij}a_i^*a_j^*(\mathbf{a}_i\cdot\mathbf{a}_j)$.

Table VI. Selected Material Parameters[a] for $Cp^*W(NO)(\eta^2\text{-}S_2C(PMe_3)Ph)(Ph)\cdot CH_2Cl_2$ ($\mathbf{10}\cdot CH_2Cl_2$)

atoms	bond length (Å)	atoms	bond angle (deg)
W(1)–Cp*[b]	2.061(4)	W(1)–N(1)–O(1)	172.4(4)
W(1)–N(1)	1.753(4)	S(1)–W(1)–S(2)	69.88(4)
W(1)–C(11)	2.208(4)	W(1)–S(1)–C(17)	93.4(1)
W(1)–S(1)	2.494(1)	W(1)–S(2)–C(17)	93.4(1)
W(1)–S(2)	2.503(1)	S(1)–C(17)–S(2)	102.9(2)
N(1)–O(1)	1.224(5)	S(1)–C(17)–P(1)	106.5(2)
C(17)–S(1)	1.833(4)	S(2)–C(17)–P(1)	105.9(2)
C(17)–S(2)	1.825(4)	P(1)–C(17)–C(21)	109.9(2)
C(17)–C(21)	1.526(6)	S(1)–C(17)–C(21)	114.9(3)
C(17)–P(1)	1.823(4)	S(2)–C(17)–C(21)	115.9(3)

[a] Esd's are given in parentheses. [b] Cp* refers to the centroid of the pentamethylcyclopentadienyl ligand.



(1)

M = Mo or W; aryl = Ph or p-tolyl

X,Y = S,S (**1**-**3**) or N-p-tolyl, O (**4**-**6**) or O,O (**7**)

The diphenyl complex $Cp^*W(NO)Ph_2$ also reacts with diphenylketene, but in this case no organometallic product can be isolated. However, workup of the reaction solution results in the isolation of diphenylmethyl phenyl ketone from Et_2O as white crystals.[12] The isolation of this ketone indicates that insertion of diphenylketene into the metal–

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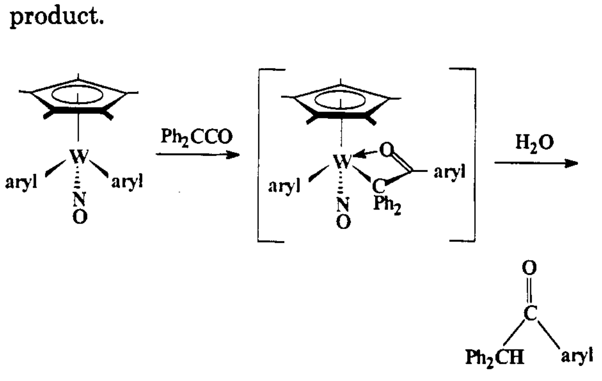
(11) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2B and 2.3.1.

aryl bond probably did occur, but the resulting insertion complex decomposed upon column chromatography (eq 2). Consistent with this rationale is the fact that similar treatment of Cp*W(NO)(*p*-tolyl)$_2$ with diphenylketene affords diphenylmethyl *p*-tolyl ketone as the only isolable product.



(2)

aryl = Ph or *p*-tolyl

Spectroscopic Characterization of Complexes 1–8. The numbering scheme, yield, and elemental analysis data for these compounds are listed in Table I, their mass spectral and IR data in Table II, and their ^{1}H and ^{13}C NMR data in Table III. All data are consistent with complexes 1–8 being monomeric, 18-valence-electron species possessing the molecular structures depicted in eq 1. Noteworthy features of this data include the following.

(1) The room-temperature ^{1}H NMR spectra of complexes 1 and 4–6 show broadened aryl proton signals, a feature which suggests that one of the two aryl groups experiences hindered rotation.[13]

(2) The ^{13}C{^{1}H} NMR spectra of 1 and 2 exhibit resonances around δ 236 ppm, assignable to the carbon of the inserted CS$_2$. These signals are comparable to carbon resonances displayed by similar thioformate[14] and thiocarboxylate[15] complexes and significantly downfield from that of free CS$_2$ (δ 192.8 ppm). In the ^{13}C{^{1}H} NMR spectra of 7 and 8, the carboxylate carbon resonates at δ 168.3 and 180.4 ppm, respectively, these values being consistent with those observed in the ^{13}C{^{1}H} NMR spectra of similar alkyl- and aryl–carboxylate compounds.[16]

(3) The ^{1}H NMR spectrum of the dark red crystals obtained from the reaction between Cp*Mo(NO)(*p*-tolyl)$_2$ and CS$_2$ consistently reveals the existence of two species in a 5:1 ratio. The major product displays spectral features similar to those of the analogous tungsten complex 2, and hence these features are attributed to complex 3. However, the nature of the minor product is presently unclear. Since the elemental analysis of the mixture is consistent with the molecular formula being Cp*Mo(NO)(*p*-tolyl)$_2$·CS$_2$, the two complexes are probably structural isomers. One possibility is that the minor product is a linkage isomer of the major product. Thus, instead of CS$_2$ being sulfur bound in a chelating fashion, Mo–η^2-S$_2$CR, as in 3, the minor product may involve coordination through the carbon of the CS$_2$ group, Mo–C(S)SR.[17] However, we have not yet effected a separation of these products in order to establish definitively the nature of this minor product.

(4) The ν_{NO}'s exhibited by complexes 1–8 in their IR spectra (Table II) are nearly identical (within 6 cm^{-1}) to the ν_{NO}'s of the parent diaryl complexes. These findings suggest that back-bonding to the π^*-acceptor orbital of the modified heterocumulene ligand may well compete with the π^*-acceptor orbital of the nitrosyl ligand for the metal's electron density.[18]

(5) The IR spectra of compounds 7 and 8 contain bands attributable to symmetric and asymmetric CO$_2$ stretches. However, these spectra exhibit no bands in the region between 1800 and 1600 cm^{-1} diagnostic of η^1-bound carboxylates.[19] Furthermore, the values for $\Delta\nu_{CO_2}$ are 118 and 51 cm^{-1}, respectively, which strongly support the formulation of these complexes as containing η^2-carboxylate ligands.[20]

(6) Two CS$_2$ stretching modes are evident in the IR spectra of the η^2-thiocarboxylate complexes 1–3. The asymmetric CS$_2$ stretches occur between 1176 and 1174 cm^{-1}, whereas the lower energy symmetry CS$_2$ stretching frequencies are between 1021 and 1005 cm^{-1}. These CS$_2$ stretching modes are consistent with those observed for other η^2-thiocarboxylate complexes.[15,21]

Relative Ease of Insertion. We find that for the Cp*W(NO)(aryl)$_2$ systems the ease of heterocumulene insertion diminishes qualitatively in the order carbon disulfide > isocyanate > carbon dioxide, a trend consistent with that found for the related Cp$_2$ZrR$_2$ (R = alkyl or aryl) complexes by Floriani and co-workers.[22] Also, there is no noticeable dependence of the qualitative rate of insertion on the nature of the aryl group in the diaryl organometallic reactants.

Reactivity Studies. With the expectation that the heterocumulene-inserted complexes 1–7 should display additional reactivity that will allow further functionalization, we have effected the following preliminary reactivity studies.

(a) Protonolysis. For these studies, 4 was selected as the model heterocumulene-inserted complex primarily for two reasons, namely (1) it is easily prepared and (2) its hydrolysis product, *p*-tolylbenzamide is innocuous and readily identifiable spectroscopically. The reactions of complex 4 with water, acetic acid-*d*$_4$, and hydrochloric acid give Cp*W(O)$_2$Ph, Cp*W(NO)(η^2-O$_2$CCD$_3$)(Ph) (9), and Cp*W(NO)Cl$_2$, respectively, as the organometallic products. In all cases, the organic product is *p*-tolylbenzamide, which has been isolated and fully characterized.[8] The physical properties of 9 closely resemble those

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[12] Diphenylmethyl phenyl ketone: IR (Nujol mull) ν_{CO} 1681 cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ 7.97 (d, J = 6.9 Hz, 2H, *o* Ar *H*), 7.23 (d, J = 6.3 Hz, 4H, *o* Ar *H*), 7.10–6.90 (m, 9H, Ar *H*), 5.87 (s, 1H, C*H*); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 197.7 (*C*=O), 139.8, 139.7, 132.8, 129.6, 129.1, 128.9, 128.7, 127.2 (*C*$_{arom}$), 59.6 (Ph$_2$CH); low-resolution mass spectrum (probe temperature 200 °C) *m/z* 272 ([P]$^+$). Anal. Calcd for C$_{20}$H$_{16}$O: C, 88.20, H, 5.92. Found: C, 88.40; H, 5.91.

[13] Similar phenomena have been observed with related systems involving carbon monoxide insertion; see: Debad, J. D.; Legzdins, P.; Einstein, F. W. B.; Batchelor, R. J. *Organometallics* **1993**, *12*, 2094.

[14] Darensbourgh, D. J.; Rokicki, A. *Organometallics* **1982**, *1*, 1685.

[15] Scott, F.; Kruger, G. J.; Cronje, S.; Lombard, A.; Raubenheimer, H. G.; Benn, R.; Rufinska, A. *Organometallics* **1990**, *9*, 1071.

[16] (a) Cutler, A.; Raja, M.; Todaro, A. *Inorg. Chem.* **1987**, *26*, 2877. (b) Holl, M. M.; Hillhouse, G. L.; Folting, K.; Huffman, J. C. *Organometallics* **1987**, *6*, 1522.

[17] In contrast, CS$_2$ insertions into metal alkoxides and amides generally give only products of the form M–SC(S)R. See, for example: Glueck, D. S.; Newman Winslow, L. J.; Bergman, R. G. *Organometallics* **1991**, *10*, 1462.

[18] Jorgensen, W. L.; Salem, L. *The Organic Chemist's Book of Orbitals*; Academic: New York, 1974.

[19] (a) Smith, S. A.; Blake, D. M.; Kubota, M. *Inorg. Chem.* **1972**, *11*, 660. (b) Bradley, M. G.; Roberts, D. A.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1981**, *103*, 379.

[20] Darensbourg, D. J.; Grotsch, G.; Wiegreffe, P.; Rheingold, A. *Inorg. Chem.* **1987**, *26*, 3827.

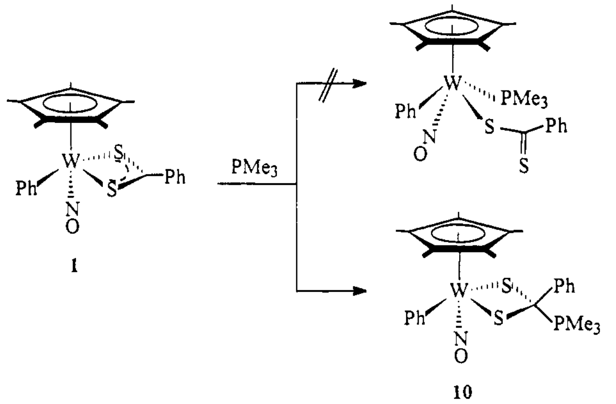
[21] (a) Yaneff, P. V. *Coord. Chem. Rev.* **1977**, *23*, 183. (b) Werner, H.; Bertleff, W. *Chem. Ber.* **1980**, *113*, 267. (c) Torres, M. R.; Perales, A.; Ros, J. *Organometallics* **1988**, *7*, 1223.

[22] Gambarotta, S.; Strologo, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1985**, *24*, 654.

displayed by the related complex 8 (vide supra). The dioxo organometallic product resulting from treatment of 4 with water is typical of the reaction of water with Cp′W(NO)(aryl)$_2$.[9] The reaction of 4 with an excess of acetic acid-d_4 confirms that the proton of the liberated amide originates from the protonic acid. Thus, the low-resolution mass spectrum of the final reaction mixture shows a parent peak for *p*-tolylbenzamide-d_1 at $[P]^+ = m/z$ 212, one mass unit larger than for the mass spectrum of the non-deuterated amide. Finally, the addition of 1 equiv of HCl to 4 was expected to generate *p*-tolylbenzamide and the known monochloro species Cp*W(NO)(Ph)(Cl). However, even at low temperatures, the dichloro complex is the only organometallic species generated from this reaction with HCl.

(b) Reactions with Lewis Bases. Formation of Cp*W(NO)(η^2-S$_2$C(PMe$_3$)Ph)(Ph) (10). In our investigations, complexes 1, 4, and 7 were treated with CO and PMe$_3$ at 1 atm in benzene-d_6 solutions in NMR tubes. In all but one case, both Lewis bases failed to form adducts at room temperature with the organometallic reactants. These observations suggest that the η^2 linkage of the inserted heterocumulene ligands to the metal centers is quite strong and is best described as being symmetrical with delocalized bonding over the three atoms defined by X, C, and Y.

The lone successful Lewis-base reaction lends further credence to the above bonding description for these complexes. Complex 1 reacts with PMe$_3$ in Et$_2$O solutions at room temperature to give 10, in which the Lewis base has attached not at the tungsten center, as might be expected, but rather at the dithiocarboxylate carbon (eq 3). Complex 10 can be isolated in good yields as orange crystals from 1:1 CH$_2$Cl$_2$/hexanes (as a CH$_2$Cl$_2$ solvate) or from 1:1 Et$_2$O/pentane. Redissolution of the crystals in a solvent (pentane, benzene, or Et$_2$O) causes a small degree of dissociation to 1 and PMe$_3$, as evidenced by a change in color to purple and the appearance of signals due to 1 in the ^{1}H NMR spectrum ($K \approx 0.7$, C$_6$D$_6$, 298 K).



(3)

The ^{1}H NMR spectrum of 10 is consistent with its formulation. As found for its parent complex 1, one phenyl group displays hindered rotation, the signal due to the ortho protons (δ 8.20 ppm) being broadened significantly. The most interesting feature of the ^{13}C{^{1}H} NMR spectrum of 10 is the resonance at δ 56.3 ppm. This doublet is assignable to the η^2-thiocarboxylate carbon, and the coupling ($^1J_{PC}$ = 54 Hz) indicates connectivity to phosphorus. The chemical shift of this carbon resonance is significantly upfield from the corresponding resonance observed in 1 (δ 236.3 ppm) and indicates a significant change from delocalized bonding to that of a tetrahedral, σ-bonded carbon.

Solid-State Molecular Structure of 10·CH$_2$Cl$_2$. An X-ray crystallograhic analysis has been performed on a single crystal of 10·CH$_2$Cl$_2$, and the ORTEP diagram of the molecular structure is shown in Figure 1 with selected intramolecular dimensions being collected in Table VI. The solid-state molecular structure confirms that the phosphine has indeed attacked the dithiolate carbon to form a phosphonium betaine ligand.[23] The PMe$_3$ unit is distal to the Cp* ring, thereby suggesting that the proximal electrophilic C(17) site in the parent complex is sterically sheltered by the bulky Cp* ligand. The P(1)–C(17) bond length of 1.823(4) Å is comparable to that found in the structurally characterized complexes [Ru(S$_2$C(PMe$_2$Ph)H)(PMe$_2$Ph)$_3$]PF$_6$,[23a] [(triphos)Co(S$_2$C(PEt$_3$)H)](BPh$_4$)$_2$,[23c] and [(triphos)Rh(S$_2$C(PEt$_3$)H)](BPh$_4$)$_2$[23e] (triphos = 1,1,1-tris((diphenylphosphino)methyl)ethane). The four-membered metallacycle (–M–S–C–S–) is both planar and symmetrical, a feature also seen in the previously mentioned complexes. The carbon–sulfur bond lengths and angles determined for 10·CH$_2$Cl$_2$ are typical of such complexes. The geometry about C(17) is tetrahedral, a change from the putative planar geometry at this carbon in the parent complex. This structural change is in accord with the ^{13}C{^{1}H} NMR chemical shifts of the signals due to that carbon in the two related complexes. The values for the W–N and N–O bond lengths as well as the W–N–O bond angle are similar to those exhibited by related tungsten mononitrosyl complexes.[24]

A valence-bond description of the bonding of 10 can be proposed on the basis of the metrical parameters existing in the molecular structure. The tetrahedral geometry about the phosphorus atom of the dithio chelate can be explained by the assignment of a formal positive charge. However, since an overall neutral charge is maintained, the complex must be zwitterionic in nature, with the formal negative charge residing on either the tungsten atom or distributed over the W–S–C–S system. The latter possibility is unlikely, since the W–S bond distances (ca. 2.50 Å) are indicative of single bonds.[25] Consistent with placement of a formal negative charge at tungsten, the low value of ν_{NO} (1548 cm^{-1}) in the IR spectrum of the complex is indicative of significant electron density at the metal center.

Further insight into the bonding of both 1 and 10 is facilitated by adopting a molecular-orbital point of view. In the case of 1, the carbon atom of the SS′ chelate is most likely planar in geometry. As a result, a considerable degree of electronic delocalization is possible due to extensive conjugation of the thiobenzoate. Consistently, ν_{NO} indicates that the tungsten center of 1 is relatively electron deficient. Furthermore, this view of the bonding predicts that the carbon of the dithiolate chelate will be highly electrophilic in nature (i.e. have a low-lying LUMO). The ν_{NO} value for complex 10 is 30 cm^{-1} lower than that of its parent complex 1, thereby indicating that the

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[23] See, for example: (a) Ashworth, T. V.; Singleton, E.; Laing, M. *J. Chem. Soc., Chem. Commun.* 1976, 875. (b) Werner, H.; Bertleff, W. *Chem. Ber.* **1990**, *113*, 267. (c) Bianchini, C.; Meli, A.; Orlandini, A. *Inorg. Chem.* **1982**, *21*, 4151. (d) Bianchini, C.; Meli, A.; Orlandini, A. *Inorg. Chem.* **1982**, *21*, 4166. (e) Bianchini, C.; Meli, A.; Dapporto, P.; Tofanari, A.; Zanello, P. *Inorg. Chem.* **1987**, *26*, 3677.

[24] For the results of the X-ray crystallographic analysis of Cp*W(NO)(*o*-tolyl)$_2$, see ref 4.

[25] Legzdins, P.; Sánchez, L. *J. Am. Chem. Soc.* **1985**, *107*, 5525.

tungsten center has become less Lewis acidic upon reaction with the Lewis base PMe_3. The carbon of the SS′ chelate in **10** displays tetrahedral geometry, which disrupts the type of conjugation possible in **1**. Though still a formula three-electron donor to the metal center, the phosphonium betaine ligand is less of a Lewis π-acid than is the thiobenzoate ligand.

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Supplementary Material Available: Tables of hydrogen atom parameters, anisotropic thermal parameters, all bond lengths and bond angles, torsion angles, intermolecular contacts, and least-squares planes for the complex **10**·CH_2Cl_2 (16 pages). Ordering information is given on any current masthead page.

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