

presence or absence of $\text{CH}_2=\text{CHCH}_2\text{MgBr}$, suggesting that the added MgBr_2 had an active role in the addition reaction. One possibility, as outlined in Scheme II, is that chloride loss from an intermediate cyclopentadiene complex such as **B** is facilitated by the ability of a magnesium dihalide to stabilize a potentially unsaturated intermediate as shown in **C**. The double halide bridge in **C** could result in halide exchange concurrent with hydrogen migration from the cyclopentadiene ligand to the metal to give **11**. We have no direct evidence for initial magnesium halide complexation of **2**, but Lewis acid complexation of a chloride in **2** to form **A** would be a natural first step in the sequence and should enhance the electrophilicity of the cyclopentadienyl ligand.

Conclusion

The results above establish that the nucleophilic alkyls in some Grignard reagents can be induced to add cleanly and in high yield to a cyclopentadienyl ligand in $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$. These reactions

offer convenient access to tungstenocene derivatives containing functionalized cyclopentadienyl ligands and suggest that the potential of nucleophilic alkylation as an approach to the functionalization of cyclopentadienyl ligands should be explored in other systems. Further experiments along these lines, and exploring the factors controlling the regioselectivity of a variety of nucleophiles with **2**, are underway in our laboratories.

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Registry No. **2**, 12184-26-8; **3**, 121524-53-6; **4**, 121524-54-7; **5**, 121524-55-8; **6**, 121524-56-9; **7**, 121524-57-0; **8**, 121524-58-1; **9**, 61089-07-4; **10**, 121524-59-2; **11**, 121524-60-5; $\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{Br}_2$, 12184-19-9; $\text{CH}_2=\text{CHCH}_2\text{MgCl}$, 2622-05-1; MgCl_2 , 7786-30-3; PhCH_2MgCl , 6921-34-2; $(\text{CH}_3)_3\text{SiCH}_2\text{Li}$, 1822-00-0; $(\text{CH}_3)_3\text{SiCH}_2\text{MgCl}$, 13170-43-9; $\{(\text{CH}_3)_3\text{SiCH}_2\}_2\text{Mg}$, 51329-17-0; $\text{CH}_2=\text{CHCH}_2\text{MgBr}$, 1730-25-2; $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{MgCl}$, 5674-01-1.

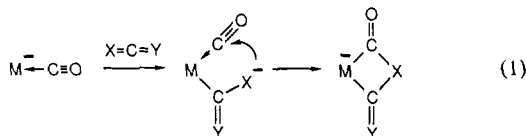
Formation of Metalloheterocycles by Addition of Heteroallenes to the Electron-Rich Carbonyl Complex $[\text{W}(\eta\text{-C}_5\text{H}_5)_2(\text{CO})]$

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Abstract: The reactions of $[\text{W}(\eta\text{-C}_5\text{H}_5)_2(\text{CO})]$ (**1**) with a range of heteroallenes establish that four-membered metallocycles can be formed by addition of heteroallenes to an electron-rich neutral carbonyl complex. Metallocycloimides $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\{\text{C}(\text{O})\text{N}(\text{R})\text{C}(\text{O})\}]$ (**2**, $\text{R} = \text{CH}_3$; **3**, $\text{R} = \text{Ph}$) are formed by addition of methyl and phenyl isocyanate to **1**, and the metallocycloacylamidine $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\{\text{C}(\text{O})\text{N}(\text{Ph})\text{C}(\text{NPh})\}]$ (**4**) is formed by addition of diphenylcarbodiimide to **1**. In surprising contrast, addition of phenyl isothiocyanate to **1** leads to formation of a four-membered metallocycle determined by single-crystal X-ray diffraction ($R_w = 3.77\%$) to be the metallocyclothioacylamidine $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\{\text{C}(\text{S})\text{N}(\text{Ph})\text{C}(\text{NPh})\}]$ (**5**). The complex crystallizes in the monoclinic space group $P2_1/n$ with $a = 7.816$ (2) Å, $b = 19.838$ (5) Å, $c = 13.066$ (3) Å, $\beta = 92.33$ (2)°, $d_{\text{calcd}} = 1.81 \text{ g mL}^{-1}$, $Z = 4$. It is proposed that initial $\text{S}=\text{C}=\text{NPh}$ addition to **1** results in ring closure through S to give a metallocycle which eliminates COS (GC) to form an intermediate isonitrile complex. Addition of a second $\text{S}=\text{C}=\text{NPh}$ with ring closure through N then leads to **5**. There is a fine balance between ring closure through S and N in isothiocyanate addition to **1**, and $\text{S}=\text{C}=\text{NCH}_3$ forms predominantly the metallocycloacylthioamide $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\{\text{C}(\text{S})\text{N}(\text{CH}_3)\text{C}(\text{O})\}]$ (**8**) in diethyl ether and a mixture of **8** (53%) and the bis adduct $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\{\text{C}(\text{NCH}_3)\text{N}(\text{CH}_3)\text{C}(\text{S})\}]$ (**9**) (27%) in pentane.

It is now well-established that coordination of heteroallenes to anionic transition-metal complexes containing carbonyl ligands can result in incorporation of heteroallenes into metallocycles as shown in eq 1. In the case of CO_2 , for example, we have



suggested that the accessibility of metalloanhydrides ($\text{X} = \text{Y} = \text{O}$) is responsible for the facile scrambling of labeled oxygens between coordinated CO_2 and coordinated CO in $\eta^1\text{-C}$ complexes of CO_2 with $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]^{-3}$ and $[\text{W}(\text{CO})_5]^{2-4}$. Fehlhammer and his co-workers have also established that metallocycles are the ground-state structures of complexes of salts of $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]^{-}$ with carbodiimides ($\text{RN}=\text{C}=\text{NR}$; $\text{R} =$

$i\text{-Pr}$, $t\text{-Bu}$, C_6H_{11} , Ph)⁵ and ketenimines ($\text{R}_2\text{C}=\text{C}=\text{NR}'$; $\text{R} = \text{Ph}$, $\text{R}' = \text{CH}_3$; $\text{R} = \text{CH}_3$, $\text{R}' = \text{Ph}$)⁶ and that the $\eta^1\text{-C}$ complex of the isothiocyanate CH_3NCS with $\text{Na}[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]$ is in equilibrium with the metallocycle $\text{Na}[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})\{\text{C}(\text{S})\text{N}(\text{CH}_3)\text{C}(\text{O})\}]$.⁷

Fehlhammer's results suggested that, under some circumstances, the addition of CO_2 to CO complexes might lead to the formation of isolable metalloanhydride complexes analogous to those which we had proposed as reactive intermediates, and this has led us to further examine the reactivity of CO_2 and other heteroallenes with electron-rich carbonyl complexes. We were particularly interested in the possibility that metallocycles might be more stable if they were formed by the addition of heteroallenes to a CO complex which, although nucleophilic, was not anionic, and the tungsten complex $[\text{W}(\eta\text{-C}_5\text{H}_5)_2(\text{CO})]$ (**1**)⁸ was a promising

(5) (a) Fehlhammer, W. P.; Mayr, A.; Ritter, M. *Angew. Chem., Int. Ed. Engl.* 1977, 16, 641. (b) Fehlhammer, W. P.; Christian, G.; Mayr, A. *J. Organomet. Chem.* 1980, 199, 87.

(6) Fehlhammer, W. P.; Hirschmann, P.; Mayr, A. *J. Organomet. Chem.* 1982, 224, 153.

(7) Fehlhammer, W. P.; Mayr, A. *J. Organomet. Chem.* 1980, 191, 153.

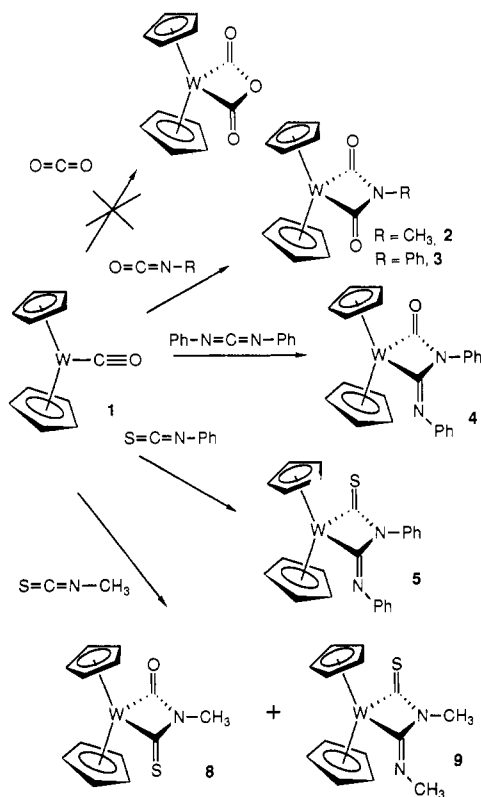
(8) (a) Thomas, J. L. *J. Am. Chem. Soc.* 1973, 95, 1838. (b) Green, M. L. H.; Francis, B. R.; Luong-thi, T.; Moser, G. A. *J. Chem. Soc., Dalton Trans.* 1976, 1339.

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(3) Lee, G. R.; Cooper, N. J. *Organometallics* 1985, 4, 794.

(4) Maher, J. M.; Lee, G. R.; Cooper, N. J. *J. Am. Chem. Soc.* 1982, 104, 6797.

Scheme I. Products of Heteroallene Addition to $[W(\eta\text{-C}_5\text{H}_5)_2(\text{CO})]$ 

substrate for such reactions since it has been reported to react with methyl iodide to give $[W(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CH}_3)]^+.$ ⁹ Although we have established that 1 does not form a metalloanhydride with CO_2 , it does form a number of other metalloheterocycles by addition of heteroallenes including isocyanates, isothiocyanates, and carbodiimides, as summarized in Scheme I. We have published a preliminary communication on the formation of the metallocycloimides 2, 3 by addition of isocyanates to 1,¹⁰ and we now wish to report details of those experiments and of the other reactions summarized in Scheme I. These provide the first examples of metalloheterocycle formation by heteroallene addition to a neutral carbonyl complex of a transition metal.

Experimental Section

General Data. All transformations and manipulations involving air-sensitive compounds were performed by using either standard Schlenk techniques or a Vacuum Atmospheres drybox under an atmosphere of prepurified nitrogen or argon unless otherwise noted. Glassware was either flame dried under vacuum or dried in an oven (>4 h, 120°C) before use. Tetrahydrofuran (THF) and diethyl ether were predried over sodium wire and then distilled from sodium/benzophenone ketyl under nitrogen. Pentane was stirred for 2 days over concentrated sulfuric acid and then over solid K_2CO_3 for 6 h before being distilled from LiAlH_4 under nitrogen. Reagent grade acetone (Mallinckrodt) was used as received. The complex $[W(\eta\text{-C}_5\text{H}_5)_2(\text{CO})]$ (1) (40% yield) was prepared by a literature procedure,^{8b} but in our hands this material was consistently contaminated with 5–10% $[W(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]$. Methyl isocyanate (Aldrich), phenyl isocyanate (Aldrich), and phenyl isothiocyanate (Aldrich) were all used as received. Methyl isothiocyanate (Aldrich) was distilled under nitrogen from phosphorus pentasulfide and stored as a THF solution under argon. Carbon dioxide (Matheson) and carbonyl sulfide (Matheson) were also used as received. Diphenylcarbodiimide was prepared by the literature method.¹¹

¹H NMR spectra were recorded on a Bruker AM-300 (300 MHz) or a Bruker WM-300-WB (300 MHz) NMR spectrometer. Perdeuterioacetone, -acetonitrile, -dimethyl sulfoxide, and -dichloromethane (all 99.5+ atom %) were purchased from Merck, Sharpe, and Dohme or from Cambridge Isotopes and were used as received. Chemical shifts are

reported in δ using the residual proton resonances of the deuterated solvents as an internal standard. ¹³C NMR spectra were obtained on a Bruker AM-300 (75.5 MHz) or a Bruker WM-300-WB (75.5 MHz) NMR spectrometer. Chemical shifts are reported in δ with use of the ¹³C chemical shift of the deuterated solvent as an internal standard. Infrared spectra were obtained as KBr pellets on a Perkin-Elmer 683 grating infrared spectrometer, by using the 1601-cm^{-1} band of polystyrene as an external reference. Mass spectra were recorded on a Kratos MS-9 mass spectrometer. Mass spectral patterns which exhibited the W isotope envelope are reported as the values of m/e which correspond to the species containing the ¹⁸⁴W isotope. Microanalyses were carried out as indicated by Schwarzkopf Microanalytical Laboratory, Woodside, NY (Sch) or by Galbraith Microanalytical Laboratory, Knoxville, TN (Gal). Gas chromatographic analyses were performed on a Perkin-Elmer Sigma-300. A thermal conductivity detector and a $3\text{ ft} \times 1/8$ in. Teflon column packed with 80/100 mesh Poropak Q (Alltech) were used for the analysis of carbon dioxide and carbonyl sulfide.

X-ray Crystallography. Crystals for X-ray diffraction studies were mounted in glass capillary tubes (Charles Supper Co.) and flame sealed under argon. Data were collected on a Nicolet R3 diffractometer by using graphite monochromatized Mo $K\alpha$ radiation (50 kV, 30 mA). Data collection was controlled by the Nicolet P3 program,¹² and structures were solved with SHELXTL.¹³ Diffractometer data were processed with FOXTAPE, a local modification of the Nicolet program XTAPE. Empirical absorption corrections were performed by the program XEMP (Nicolet), while drawings were generated by the program SNOOP (part of the Oxford University CHEMGRAF Suite package) or by XPLOT (Nicolet). All molecular calculations were performed with the aid of the program XP (Nicolet). Atomic scattering factors were based on literature values for W¹⁴ and on those in the SHELXTL program for other atoms. Weights were taken as $[\sigma^2(F) + gF^2]^{-1}$.

$[W(\eta\text{-C}_5\text{H}_5)_2][C(O)N(CH_3)C(O)]$ (2). A dark green slurry of $[W(\eta\text{-C}_5\text{H}_5)_2(\text{CO})]$ (0.65 g, 1.90 mmol) in pentane (60 mL) was treated with 13.0 mL of CH_3NCO (12.6 g, 220.9 mmol) with rapid stirring. Over the course of 2.5 h, the solution color changed to a bright orange and spectroscopically pure $[W(\eta\text{-C}_5\text{H}_5)_2][C(O)N(CH_3)C(O)]$ was deposited as an orange powder. The complex was collected by decantation, washed with pentane (3×20 mL), and vacuum dried (0.67 g, 1.68 mmol = 88%). Analytically pure material could be obtained as irregular needles and spars (ca. 90% recovery) by slow cooling to -70°C of a saturated acetone solution of the complex. *Note:* Crystalline samples for analysis were dried under high vacuum for a minimum of 48 h to remove occluded water: ¹H NMR (300 MHz, acetonitrile- d_3) δ 4.91 (s, 10 H, $2C_5H_5$), 2.34 (s, 3 H, NCH_3); ¹³C NMR (75.5 MHz, gated decoupled, dimethyl sulfoxide- d_6) δ 176.2 (s, satellites $J_{183W-C} = 93.4$ Hz, $2[W-C(O)]$), 83.6 (d, $J_{C-H} = 183.2$ Hz, $2C_5H_5$), 22.8 (q, $J_{C-H} = 137.7$ Hz, CH_3); IR (KBr) 3100 ms, 2930 w br, 2865 w, 1721 m, 1679 ms, 1663 ms, 1605 s br, 1411 ms, 1391 ms, 1364 w, 1304 s br, 1254 ms, 1103 mw, 1065 w br, 1011 m, 995 m, 948 ms br, 896 ms, 839 ms, 792 m, 770 m, 609 ms, 601 ms, 485 mw br, 419 m, 378 m cm^{-1} ; Mass spectrum (parent ion, ¹⁸⁴W) m/e 399. Anal. Calcd for $C_{11}H_{13}N_2O_2W$: C, 39.12; H, 3.29; N, 3.51. Found (Sch): C, 39.06; H, 3.37; N, 3.58.

$[W(\eta\text{-C}_5\text{H}_5)_2][C(O)N(Ph)C(O)]$ (3). A dark green slurry of $[W(\eta\text{-C}_5\text{H}_5)_2(\text{CO})]$ (0.25 g, 0.73 mmol) in pentane (25 mL) was treated with 3.0 mL of PhNCO (3.27 g, 27.4 mmol) with stirring. Reaction was instantaneous, as evidenced by a rapid solution color change to orange and the immediate deposition of $[W(\eta\text{-C}_5\text{H}_5)_2][C(O)N(Ph)C(O)]$ as a pale orange powder. After 1 h, the complex was collected by decantation, washed with pentane (3×20 mL), and dried in vacuo (0.32 g, 0.69 mmol = 95%). ¹H NMR (300 MHz, acetone- d_6) δ 7.40–7.05 (c, 5 H, C_6H_5), 5.11 (s, 10 H, $2C_5H_5$); ¹³C NMR (75.5 MHz, broad band decoupled, 0 $^\circ\text{C}$, dichloromethane- d_2) δ 176.6 (s, satellites $J_{183W-C} = 91.6$ Hz, $2[W-C(O)]$), 134.5 (s, C_6H_5 -ipso), 128.7, 123.7 (both s, C_6H_5 -ortho, -meta), 126.0 (s, C_6H_5 -para), 84.4 (s, $2C_5H_5$); IR (KBr) 3100 m, 3065 m, 1709 ms, 1625 s br, 1594 ms sh, 1579 m, 1545 mw, 1489 m br, 1452 m, 1428 mw, 1412 mw, 1384 mw, 1292 s br, 1178 mw, 1110 ms, 1091 ms, 1048 m, 1012 w, 990 w, 909 mw, 841 m, 778 m, 745 ms, 696 ms, 628 m, 610 m, 601 m, 558 m, 499 m, 390 mw cm^{-1} . Anal. Calcd for $C_{15}H_{15}N_2O_2W$: C, 46.87; H, 3.28; N, 3.04. Found (Gal): C, 47.10; H, 3.30; N, 3.15.

$[W(\eta\text{-C}_5\text{H}_5)_2][C(O)N(Ph)C(NPh)]$ (4). To a dark green solution of $[W(\eta\text{-C}_5\text{H}_5)_2(\text{CO})]$ (0.29 g, 0.85 mmol) in diethyl ether (25 mL) was added 3.0 mL of diphenylcarbodiimide (3 g, 15 mmol) with stirring.

(12) *P3/R3 Data Collection Manual*; Nicolet Instruments Corp.: Madison, WI, 1983.

(13) Sheldrick, G. M. *SHELXTL User Manual, Revision 4*; Nicolet Instrument Corp.: Madison, WI, 1983.

(14) *International Tables for X-ray Crystallography*; Ibers, J., Hamilton, J. C., Eds.; Kynoch: Birmingham, England, 1974; Vol. IV, pp 72–98.

(9) Green, M. L. H.; Mahtab, R. *J. Chem. Soc., Dalton Trans.* **1979**, 262.

(10) Jernakoff, P.; Cooper, N. J. *J. Am. Chem. Soc.* **1987**, *109*, 2173.

(11) Campbell, T. W.; Monagle, J. S. *Organic Synthesis*; Wiley: New York, 1973; Collect. Vol. 5, p 501.

Over a 2-h period, the solution color changed to orange, and spectroscopically pure $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{C}(\text{O})\text{N}(\text{Ph})\text{C}(\text{NPh})]$ was deposited as a yellow powder. The solid was collected by decantation, washed with diethyl ether (3×20 mL), and dried in vacuo (0.43 g, 0.80 mmol = 94%). Analytically pure material could be obtained as yellow flakes (ca. 35% recovery) via slow cooling to -70°C of a saturated acetone solution of the complex: ^1H NMR (300 MHz, dimethyl sulfoxide- d_6) δ 7.46–6.77 (c, 10 H, $2\text{C}_6\text{H}_5$), 4.98 (s, 10 H, $2\text{C}_5\text{H}_5$); ^{13}C NMR (75.5 MHz, broad band decoupled, 0°C , dichloromethane- d_2) δ 172.7 (s, W-C(O)), 154.5, 154.3, 135.6 (all s, $2(\text{C}_6\text{H}_5\text{-ipso}) + \text{W-C}(\text{NPh})$), 128.6, 128.4, 125.3, 121.0 (all s, $2(\text{C}_6\text{H}_5\text{-ortho, -meta})$), 125.9, 121.9 (both s, $2(\text{C}_6\text{H}_5\text{-para})$), 84.1 (s, $2\text{C}_5\text{H}_5$); IR (KBr) 3132 mw, 3114 mw, 3089 m, 3060 mw, 3031 mw, 1674 s, 1595 vs br, 1487 s, 1453 m, 1448 m, 1412 ms, 1386 mw, 1364 ms, 1321 ms sh, 1305 s br, 1250 ms, 1174 mw, 1161 m, 1153 m, 1131 s, 1101 s, 1071 ms, 1026 mw, 1014 m, 990 ms, 942 w, 921 mw, 899 ms, 882 m, 861 ms, 839 ms, 816 m, 780 s, 761 s, 739 s, 704 s, 698 s, 625 mw, 603 ms, 592 ms, 583 ms, 548 mw, 535 ms, 500 ms, 478 w, 430 m, 403 mw sh, 389 m, 337 m sh, 327 m cm^{-1} . Anal. Calcd for $\text{C}_{24}\text{H}_{20}\text{N}_2\text{OW}$: C, 53.75; H, 3.77; N, 5.22. Found (Gal): C, 53.75; H, 3.63; N, 5.38.

$[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{C}(\text{S})\text{N}(\text{Ph})\text{C}(\text{NPh})]$ (5). A dark green solution of $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{CO}]$ (0.27 g, 0.79 mmol) in diethyl ether (20 mL) was treated with 2.5 mL of PhNCS (2.82 g, 20.9 mmol) with stirring. Reaction was immediate as evidenced by a solution color change to orange and the deposition of spectroscopically pure $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{C}(\text{S})\text{N}(\text{Ph})\text{C}(\text{NPh})]$ as a dark orange powder. After 4 h the complex was collected by decantation, washed with diethyl ether (4×20 mL), and dried in vacuo (0.37 g, 0.67 mmol = 85%). Analytically pure material could be obtained as small orange-red flakes (ca. 30% recovery) via slow cooling to -70°C of a saturated acetone solution of the complex: ^1H NMR (300 MHz, dimethyl sulfoxide- d_6) δ 7.40–6.80 (c, 10 H, $2\text{C}_6\text{H}_5$), 5.02 (s, 10 H, $2\text{C}_5\text{H}_5$); ^{13}C NMR (75.5 MHz, broad band decoupled, 0°C , dichloromethane- d_2) δ 221.2 (s, W-C(S)), 153.3, 150.3, 138.6 (all s, $2(\text{C}_6\text{H}_5\text{-ipso}) + \text{W-C}(\text{NPh})$), 128.7, 127.1, 120.6 (all s, $2(\text{C}_6\text{H}_5\text{-ortho, -meta})$), 127.5, 122.4 (both s, $2(\text{C}_6\text{H}_5\text{-para})$), 86.4 (s, $2\text{C}_5\text{H}_5$); IR (KBr) 3080 m, 3045 mw, 1612 s, 1587 s, 1453 ms, 1448 w, 1443 mw, 1409 m, 1390 mw, 1356 mw, 1325 s, 1308 m sh, 1244 m sh, 1236 m, 1199 s, 1168 m sh, 1100 ms, 1085 m sh, 1063 m, 1028 mw, 1011 mw, 988 m, 943 mw, 922 w, 909 w, 899 mw, 890 m, 879 m, 860 m, 847 mw, 834 m, 812 w, 774 m, 763 m, 750 m, 704 s, 599 w, 574 m, 549 ms, 520 m, 496 w, 465 w, 416 w, 400 w, 382 m cm^{-1} . Anal. Calcd for $\text{C}_{24}\text{H}_{20}\text{N}_2\text{SW}$: C, 52.18; H, 3.66. Found (Sch): C, 52.19; H, 3.74.

$[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{C}(\text{O})\text{N}(\text{CH}_3)\text{C}(\text{S})]$ (8). A 3.06 M solution of CH_3NCS in THF (12.0 mL = 36.7 mmol) was added to a dark green solution of $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{CO}]$ (0.71 g, 2.08 mmol) in diethyl ether (20 mL) with stirring. After 17 h, the solution color had changed to a cherry-red, and spectroscopically pure $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{C}(\text{O})\text{N}(\text{CH}_3)\text{C}(\text{S})]$ had been deposited as a rust-orange powder. The complex was collected by decantation, washed with diethyl ether (2×10 mL), and dried in vacuo (0.59 g, 1.42 mmol = 68%). Analytically pure material could be obtained as small orange-red flakes (ca. 60% recovery) via slow cooling to -70°C of a saturated diethyl ether/tetrahydrofuran solution (v/v 13:1) of the complex: ^1H NMR (300 MHz, acetone- d_6) δ 5.01 (s, 10 H, $2\text{C}_5\text{H}_5$), 2.71 (s, 3 H, NCH_3); ^{13}C NMR (75.5 MHz, gated decoupled, 0°C , dichloromethane- d_2) δ 228.9 (s, W-C(S)), 171.1 (s, W-C(O)), 86.0 (d, $^1J_{\text{C-H}} = 183.2$ Hz, $2\text{C}_5\text{H}_5$), 28.9 (q, $^1J_{\text{C-H}} = 139.9$ Hz, NCH_3); IR (KBr) 3120 mw, 3085 m, 2925 mw, 1800 mw, 1734 m, 1672 s br, 1643 s sh, 1448 mw, 1435 mw, 1410 s, 1398 s, 1372 m, 1332 s, 1235 s br, 1070 s br, 1012 m, 980 m, 930 s, 891 m, 868 ms, 836 ms, 804 m, 718 ms, 607 ms, 596 m, 582 ms, 512 w, 478 ms, 410 s, 386 ms, 354 m cm^{-1} ; mass spectrum (parent ion ^{184}W) m/e 415. Anal. Calcd for $\text{C}_{13}\text{H}_{13}\text{NOSW}$: C, 37.61; H, 3.16; N, 3.37. Found (Gal): C, 37.76; H, 3.38; N, 3.35.

X-ray Diffraction Study of $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{C}(\text{S})\text{N}(\text{Ph})\text{C}(\text{NPh})]$. Bright orange parallelepipeds of $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{C}(\text{S})\text{N}(\text{Ph})\text{C}(\text{NPh})]$ were grown by slow vapor diffusion (7 days) of diethyl ether into a saturated acetone solution of the complex. A crystal of dimensions $0.1 \times 0.2 \times 0.2$ mm mounted in a 0.2-mm capillary tube was used for the diffraction study. The unit cell was indexed with 15 reflections from the rotation photograph. Two angles were near 90° , and a lattice determination using both the P_3 program¹² and TRACER¹⁵ yielded a monoclinic cell. Examination of axial photographs confirmed this assignment since only the b -axis possessed mirror symmetry. A trial data collection revealed systematic absences which uniquely determined the space group as $P2_1/n$ (nonstandard setting of $P2_1/c$). The final unit cell parameters were obtained by a least-squares refinement of the angles obtained from 12 selected Friedel pairs in the range $20^\circ \leq 2\theta \leq 30^\circ$, and a single quadrant

Table I. Summary of Crystallographic Data for $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{C}(\text{S})\text{N}(\text{Ph})\text{C}(\text{NPh})]$

Crystal Data	
space group	$P2_1/n$
a (Å)	7.816 (2)
b (Å)	19.838 (5)
c (Å)	13.066 (3)
β (deg)	92.33 (2)
V (Å ³)	2024.4 (9)
Z	4
μ (cm ⁻¹)	61.39
d_c (g/mL)	1.81
T (°C)	25
λ (Å)	0.71069
Data Collection	
scan type	$2\theta/\theta$
max. 2θ (deg)	50
min. 2θ (deg)	3
scan range (deg)	1.8 (symmetrical)
scan speed (deg/min)	3.5–19.5
background/scan ratio	0.5
total reflns	4227
unique reflns	2469
$(I > 3\sigma(I), F > 3\sigma(F))$	
Agreement Factors	
final R (%) ^a	4.70
final R_w (%) ^b	3.77
goodness of fit (GOF) ^c	1.118
g value	0.00031

$$^a R = \sum |F_{\text{obsd}} - F_{\text{calcd}}| / \sum |F_{\text{obsd}}|; \quad ^b R_w = \sum \{w\}^{1/2} (F_{\text{obsd}} - F_{\text{calcd}}) / \sum \{w\}^{1/2} F_{\text{obsd}}; \quad ^c \text{GOF} = [\sum w(|F_{\text{obsd}}| - |F_{\text{calcd}}|)^2 / (N_{\text{obsd}} - N_{\text{parameters}})]^{1/2}.$$

of data $\{hkl\}: +h, +k, \pm l$ was collected. Full details of the data collection are presented in Table I. The intensities of three check reflections measured after every 60 reflections indicated no significant crystal decay after 73 h of exposure. A semiempirical absorption correction based on ψ scans from nine reflections in the range $6^\circ \leq 2\theta \leq 40^\circ$ and Lorentz and polarization corrections were applied to the data.

A sharpened Patterson map readily revealed the position of the W atom, and a difference map, calculated after refining the scale factor, the isotropic temperature factor, and the positional parameters of the W atom ($R = 18\%$) revealed the positions of the two nitrogen atoms, the sulfur atom, and 11 of the 24 carbon atoms. Least-squares refinement ($R = 12\%$) revealed the remaining 13 carbon atoms. At this point, hydrogen atoms were placed in calculated positions on the appropriate carbon atoms ($U_{\text{iso}}(\text{H}) = 1.2 \times U_{\text{iso}}(\text{C})$; $d_{\text{C-H}} = 0.96$ Å), and all non-hydrogen atoms were made anisotropic. Refinement was then performed to convergence ($\Delta/\sigma(\text{max}) \leq 0.1$) by using the blocked-cascade least-squares procedure of SHELXTL. The value of the F^2 multiplier was adjusted so that a normal probability plot¹⁶ gave a slope as close to 1.0 as possible. The largest peak in the final difference map had a density of $1.16 \text{ e}^-/\text{\AA}^3$ and was located near one of the cyclopentadienyl rings; all others had densities $< 0.88 \text{ e}^-/\text{\AA}^3$. Final atomic positional parameters for non-hydrogen atoms are presented in Table II. Anisotropic thermal parameters, calculated hydrogen parameters, least-square planes and interplanar angles, and angles about tungsten are given in Tables SI, SII, and SIII of the Supplementary Material.

Results and Discussion

Metallocycloimide Formation by Isocyanate Addition to $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{CO}]$ (1). The feasibility of heteroallene addition to **1** was initially established by the reaction of a large excess of CH_3NCO with a dark green slurry of **1** in pentane at room temperature. This resulted in precipitation of a bright orange powder which was shown by ^1H NMR to be a spectroscopically pure sample of a methyl isocyanate adduct of **1**. The most reasonable formulation of this adduct was as the metallocycloimide $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{C}(\text{O})\text{N}(\text{CH}_3)\text{C}(\text{O})]$ (**2**) shown in Scheme I, and this was confirmed by a single-crystal X-ray diffraction study of an orange-yellow cube grown by cooling a saturated acetone solution to 0°C over a 4-h period. Details of the diffraction study will not be repeated since they are available in our previous communication and in the Supplementary Material to that communication, but the study established the molecular geometry for **2** shown in Figure 1 and the dimensions listed in Tables III and IV.

(15) Lawton, S. L. TRACER II, a FORTRAN Lattice Transformation-Cell Reduction Program; Mobil Oil Corporation, Research Dept.: Paulsboro, NJ, 1967 (as adapted by Professor B. M. Foxman, Brandeis University).

Table II. Atomic Coordinates^a for the Non-Hydrogen Atoms of $[W(\eta-C_5H_5)_2C(S)N(Ph)C(NPh)]$

atom ^b	x/a	y/b	z/c
W	8004.5 (5)	8169.2 (2)	-190.4 (3)
C(1)	7251 (14)	9085 (6)	655 (8)
C(2)	6594 (12)	8038 (5)	1205 (7)
C(11)	7373 (16)	7790 (6)	-1778 (9)
C(12)	6214 (14)	7479 (7)	-1116 (8)
C(13)	5166 (14)	7993 (7)	-728 (9)
C(14)	5636 (16)	8608 (7)	-1157 (9)
C(15)	7013 (15)	8480 (7)	-1780 (9)
C(21)	10569 (13)	7769 (6)	-622 (8)
C(22)	10792 (13)	8481 (6)	-436 (10)
C(23)	10534 (14)	8599 (7)	602 (9)
C(24)	10135 (15)	7983 (7)	1060 (9)
C(25)	10127 (14)	7471 (7)	320 (9)
C(31)	6018 (13)	6929 (5)	1547 (7)
C(32)	4686 (15)	6589 (6)	1036 (9)
C(33)	4691 (18)	5907 (6)	887 (10)
C(34)	6030 (19)	5524 (7)	1263 (10)
C(35)	7398 (20)	5835 (6)	1762 (10)
C(36)	7387 (16)	6530 (6)	1921 (9)
C(41)	5546 (13)	9021 (5)	2262 (8)
C(42)	4017 (14)	9344 (6)	2039 (9)
C(43)	3074 (18)	9579 (8)	2849 (12)
C(44)	3667 (20)	9500 (8)	3847 (12)
C(45)	5148 (23)	9165 (6)	4049 (10)
C(46)	6101 (17)	8924 (5)	3247 (9)
N(1)	6457 (11)	8735 (4)	1427 (6)
N(2)	5899 (11)	7607 (4)	1791 (6)
S(1)	7392 (4)	9893 (2)	567 (3)

^aFractional atomic coordinates ($\times 10^4$). ^bSee Figure 2 for atom designations.

Table III. Bond Lengths (Å) within $[W(\eta-C_5H_5)_2C(O)N(CH_3)C(O)]$ ^a

W-C(1)	2.195 (3)	C(11)-C(12)	1.431 (5)
W-C(11)	2.234 (6)	C(12)-C(13)	1.429 (5)
W-C(12)	2.275 (4)	C(13)-C(13A)	1.403 (8)
W-C(13)	2.351 (3)	C(21)-C(22)	1.433 (6)
W-C(21)	2.241 (5)	C(22)-C(23)	1.420 (6)
W-C(22)	2.275 (4)	C(23)-C(23A)	1.387 (11)
W-C(23)	2.343 (4)	C(1)-O(1)	1.213 (5)
		C(1)-N(1)	1.393 (4)
		N(1)-C(2)	1.451 (7)

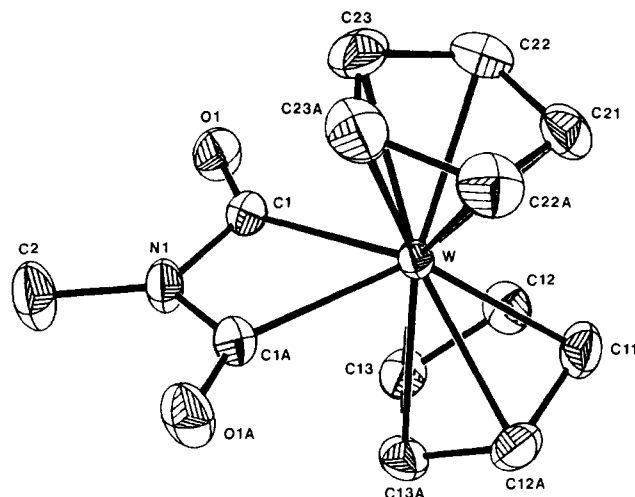
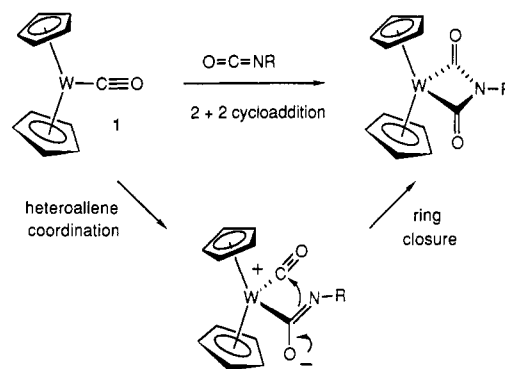
^aSee Figure 1 for atom designations.

Table IV. Bond Angles (deg) within $[W(\eta-C_5H_5)_2C(O)N(CH_3)C(O)]$ ^a

C(11)-C(12)-C(13)	106.9 (4)	W-C(1)-O(1)	139.4 (3)
C(12)-C(13)-C(13A)	108.8 (2)	W-C(1)-N(1)	97.4 (2)
C(12)-C(11)-C(12A)	108.6 (5)	N(1)-C(1)-O(1)	123.1 (3)
C(21)-C(22)-C(23)	106.5 (4)	C(1)-N(1)-C(2)	127.5 (2)
C(22)-C(23)-C(23A)	109.3 (3)	C(1)-W-C(1A)	60.3 (2)
C(22)-C(21)-C(22A)	108.4 (5)	C(1)-N(1)-C(1A)	104.7 (4)

^aSee Figure 1 for atom designations.

The diffraction study established that **2** can be described as a metallocycloimide with a metallocyclic core reminiscent of the structure of a typical organic cyclic imide.¹⁷ The metal atom, the ring carbons, and the nitrogen atom are essentially coplanar, with the maximum deviation of any one atom from the mean ring plane being 0.023 Å. The planar arrangement about nitrogen (the

**Figure 1.** Molecular structure of $[W(\eta-C_5H_5)_2C(O)N(CH_3)C(O)]$ (50% probability ellipsoids). Atoms with an A suffix are symmetry generated by the plane through the W and N atoms perpendicular to the metallocycloimide plane.**Scheme II.** Possible Mechanisms for Metallocycloimide Formation from **1**

methyl carbon is only 0.017 Å off the metallocycle plane) would suggest that the nitrogen lone pair is delocalized into the metallocycloimide framework, and, consistent with this, the nitrogen to acyl carbon bond lengths of 1.393 (4) Å are significantly shortened relative to a typical C-N single bond length of ca. 1.47 Å.¹⁸ The four-membered ring might be expected to result in a significant strain energy within the molecule, but although the N(1)-C(1)-W bond angle of 97.4 (2)° does indicate distortion of the trigonal angles about the acyl carbon, much of the compression enforced by the ring size is taken up by the C(1)-W-C(1') angle which, at 60.3 (2)°, is significantly smaller than the CWC angles of 75.4° in $[W(\eta-C_5H_5)_2CH_2CH_2H_3(CH_3)_2]^{19}$ and 75.6° in $[W(\eta-C_5H_5)_2(CH_2CH_2PMe_2Ph)CH_3]^+$,²⁰ the only other crystallographically characterized d² tungstenocene complexes with W-C σ bonds. The rather large value of 139.4 (3)° for the W-C(1)-O(1) angle probably reflects nonbonding interactions (W...O(1) = 3.215 Å) between the acyl oxygens and the non-bonding pair of electrons on the metal center, which would be expected to occupy the Alcock orbital,²¹ normal to the plane that bisects the C(1)-W-C(1') angle. It is well-established that

(16) Abrahams, S. C. *Acta Crystallogr.* **1974**, *B30*, 261.

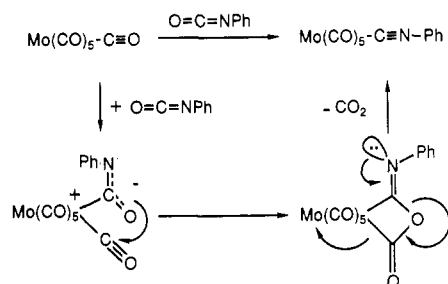
(17) (a) Mason, R. *Acta Crystallogr.* **1961**, *14*, 720. (b) Matzat, von E. *Acta Crystallogr., Sect. B* **1972**, *B28*, 415. (c) Allen, F. H.; Trotter, J. *J. Chem. Soc. B* **1971**, 1073. (d) Argay, G.; Carstensen-Oeser, E. *Acta Crystallogr.* **1973**, *B29*, 1186. (e) Baudour, P. J. L.; Messenger, J. C. *Acta Crystallogr.* **1971**, *B27*, 799. (f) Epstein, J. W.; McKenzie, T. C.; Lovell, M. F.; Perkinson, N. A. *J. Chem. Soc., Chem. Commun.* **1980**, 314. (g) Bulgarovskaia, I. V.; Novakovskaia, L. A.; Federov, I. G.; Zvonkova, Z. V. *Kristallografiya* **1976**, *21*, 515. (h) Bulgarovskaia, I. V.; Smelianskaia, E. M.; Federov, I. G.; Zvonkova, Z. V. *Kristallografiya* **1977**, *22*, 184. (i) Bulgarovskaia, I. V.; Zvonkova, Z. V.; Kolniov, O. V. *Kristallografiya* **1978**, *23*, 1175.

(18) *Tables of Interatomic Distances and Configuration in Molecules and Ions*; Special Publications 11 and 18, Sutton, L. E., Ed.; The Chemical Society: London, 1958 and 1965.

(19) Prout, K.; Jefferson, I. W.; Forder, R. A. *Acta Crystallogr., Sect. B* **1975**, *B31*, 618.

(20) Prout, K.; Gale, G. D.; Forder, R. A. *Acta Crystallogr., Sect. B* **1975**, *B31*, 307.

(21) (a) Alcock, N. W. *J. Chem. Soc. A* **1967**, 2001. (b) Green, J. C.; Green, M. L. H.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1972**, 421. (c) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

Scheme III. Probable Mechanism for the Formation of an Isocyanide Ligand by Addition of an Isocyanate to $[\text{Mo}(\text{CO})_6]$ 

electrons in this orbital are stereochemically active in d^1 and d^2 bent metallocene complexes.²²

Formation of metallocycloimides from **1** is not limited to methylisocyanate, and a dark green slurry of **1** in pentane reacted readily with excess PhNCO at room temperature to deposit a dull orange powder which was readily established by ^1H NMR to have the composition expected for an adduct of **1** with PhNCO . Formulation of this as $[\text{W}(\eta\text{-C}_5\text{H}_5)_2[\text{C}(\text{O})\text{N}(\text{Ph})\text{C}(\text{O})]]$ (**3**) was strongly supported by comparison of the gated-decoupled ^{13}C NMR spectrum of **3** with that of **2** (Table V). Both spectra contained singlets with satellites attributable to single bond coupling to ^{183}W (14% abundance, $I = 1/2$) at δ 176.2 and 176.6, respectively, which could be assigned to the acyl carbons bonded to W. The chemical shifts of these resonances are somewhat low for acyl carbons bonded to tungsten (typically above δ 200²³), but a unique chemical shift is not unreasonable given the distortions enforced on the trigonal carbon by participation in a four-membered metallocycle and the delocalization of the nitrogen lone pair into the metallocycloimide ring.

As summarized in Scheme II there are two reasonable mechanisms for the formation of metallocycloimides **2** and **3** from **1**. The simplest mechanism would involve direct $2 + 2$ cycloaddition of the isocyanate to the metal carbonyl bond, and if this is operative the reaction is isolobal with, and closely analogous to, the $2 + 2$ addition characteristically involved in the dimerization and metathesis of heteroallenes.²⁴ It is, however, also possible that the reaction involves initial $\eta^1\text{-C}$ coordination of the isocyanates to the basic metal center. In the zwitterionic intermediate, the heteroallene is nucleophilic at the β -position and the carbonyl is electrophilic at the α -position, and subsequent ring closure would give the four-membered metaloheterocycle. Although we have no direct experimental evidence which would discriminate between these mechanisms, we felt that an $\eta^1\text{-C}$ complex is likely to be at least a transient intermediate, primarily because of the analogy with the addition of heteroallenes to $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]^-$.^{3,5-7} In the case of $\text{CH}_3\text{N}=\text{C}=\text{S}$ Fehlhämmer has established, for example, that the $\eta^1\text{-C}$ complex is in equilibrium with the metaloheterocycle,⁷ and we have reported labeling studies which suggest that the same is true for the complex of CO_2 with $\text{Na}[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]$.³ Ring closure through nitrogen probably reflects the greater strength of $\text{C}=\text{O}$ bonds as compared with $\text{C}=\text{N}$ bonds: the isomeric metallocycloisocimides contain one $\text{C}=\text{O}$ and one $\text{C}=\text{N}$ bond in place of the two $\text{C}=\text{O}$ bonds in **2** and **3**.²⁵

There are no previous reports of the formation of metallocycloimide complexes, but it seems probable that metallocycloisocimides are intermediates in the previously reported²⁶ formation of isocyanide complexes by reaction of isocyanates with carbonyls

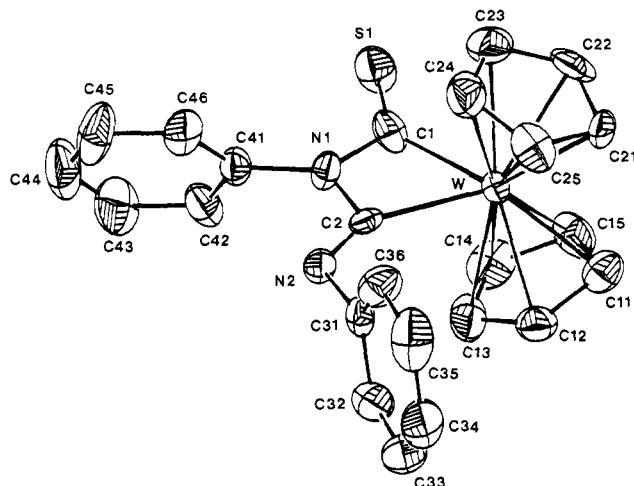


Table V. ^{13}C Resonances of Ring Carbons in Metalloheterocycles of the Type $[W(\eta\text{-C}_5\text{H}_5)_2[\text{C}(\text{X})\text{Y}(\text{Z})]]^a$

complex	δ acyl	δ iminoacyl	δ thioacyl
$[W(\eta\text{-C}_5\text{H}_5)_2[\text{C}(\text{O})\text{N}(\text{CH}_3)\text{C}(\text{O})]]$, 2	176.2		
$[W(\eta\text{-C}_5\text{H}_5)_2[\text{C}(\text{O})\text{N}(\text{Ph})\text{C}(\text{O})]]$, 3	176.6		
$[W(\eta\text{-C}_5\text{H}_5)_2[\text{C}(\text{O})\text{N}(\text{Ph})\text{C}(\text{NPh})]]$, 4	172.7	154.5 or 154.3 ^b	
$[W(\eta\text{-C}_5\text{H}_5)_2[\text{C}(\text{S})\text{N}(\text{Ph})\text{C}(\text{NPh})]]$, 5		153.3 or 150.3 ^b	221.1
$[W(\eta\text{-C}_5\text{H}_5)_2[\text{C}(\text{S})\text{N}(\text{CH}_3)\text{C}(\text{O})]]$, 8	171.1		228.9
$[W(\eta\text{-C}_5\text{H}_5)_2[\text{C}(\text{S})\text{N}(\text{CH}_3)\text{C}(\text{NCH}_3)]]$, 9		150.3	216.2

^a See Experimental Section for full ^{13}C spectra of these molecules. ^b The ipso carbons of the iminophenyls in **4** and **5** have chemical shifts similar to those of the iminoacyl carbons, and it was not possible to make definitive assignments. The solubilities of the complexes were inadequate for the observation of $^1J_{\text{W-C}}$ coupling to the iminoacyl carbons.

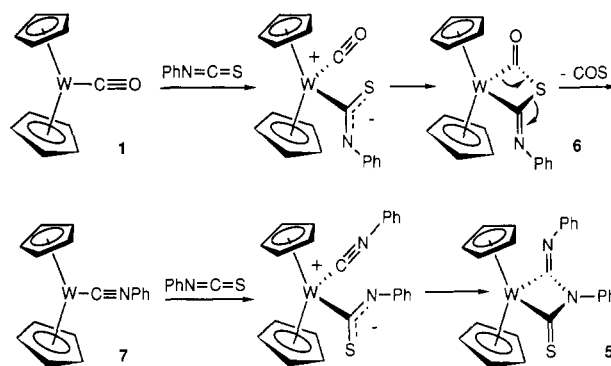
Complex **5** contains a four-membered metallocyclic ring defined by W, C(1), C(2), and N(1), and, like the metallocyclic ring in the metallocycloimide **2**, this is essentially planar with the maximum deviation of any one atom from the plane being 0.004 Å. The ring nitrogen N(1) is almost planar and lies 0.031 Å off the plane defined by C(1), C(2), and the ipso carbon C(41). This is consistent with delocalization of the nitrogen lone pair into the metallocyclic framework as indicated by the short N–C single bond distances of 1.393 (12) and at 1.416 (13) Å for the C(1)–N(1) and C(2)–N(1) bonds. These values are intermediate between the values of 1.43 Å for typical sp^2 C–N bonds and 1.333 Å in N–C=O groups.¹⁸

The dimensions of the metallocyclothioacylamidine group in **5** are similar to those of the metallocycles in the cobalt complexes $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{PMe}_3)\{\text{C}(\text{S})\text{N}(\text{Me})\text{N}(\text{R})\}]$ ($\text{R} = \text{CH}_3, \text{Ph}$),²⁷ which provide the only previously reported examples of this functional group. It is particularly interesting to note that the C(1)–W–C(2) angle of 61.9 (4)° (which is equal, within experimental error, to the analogous angle in **2**) is similar to the C–M–C angles of 67.7 (5) ($\text{R} = \text{CH}_3$) and 68.2 (4) ($\text{R} = \text{Ph}$) in the cobalt complexes, indicating that the acute value (see discussion of **2** above) is intrinsic to this functional group and is not a function of the sterically crowded environment in the tungstenocene systems. The only significant differences between the overall geometry of **5** and that of the cobalt complexes are the large values of 139.4 (6)° and 144.9 (7)° for the W–C(1)–S(1) and W–C(2)–N(2) angles. These are significantly larger than the similar Co angles and probably (as in the case of **2**) reflect nonbonding interactions ($\text{W}\cdots\text{S}(1) = 3.597$ Å, $\text{W}\cdots\text{N}(2) = 3.317$ Å) between the functionalities exo to the ring and the nonbonding electrons on the tungsten center located in the Alcock orbital (see above).

The surprising formation of **5** can be accounted for in terms of the mechanism in Scheme V, in which transient $\eta^1\text{-C}$ coordination of the isothiocyanate leads to metallocycle **6** which can generate an intermediate isonitrile complex **7** by elimination of COS. Addition of a second equivalent of isothiocyanate to **7**, probably again via an intermediate $\eta^1\text{-C}$ heteroallene complex, could lead to the observed metallocyclothioacylamidine **5**. There is no direct precedent for the formation of an isonitrile complex like **7** in this system, but **7** would be isoelectronic with **1** and is a reasonable potential intermediate. This mechanism is strongly supported by a GC study which indicated the generation of 1.1 (± 0.2) mol of COS for each mol of **1**.

The intermediacy of **7** in the formation of **5** would be consistent with Werner's previous syntheses of the cobalt complexes $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{PMe}_3)\{\text{C}(\text{S})\text{N}(\text{Me})\text{N}(\text{R})\}]$ ($\text{R} = \text{CH}_3, \text{Ph}$), by addition of isothiocyanates to the isonitrile complex $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{PMe}_3)(\text{CNCH}_3)]$.²⁷ Karin Weiss has also reported that tungsten isocyanide complexes, prepared by metathetical reactions of carbodiimides with carbene complexes $[\text{W}(\text{CO})_5\text{CPhR}]$ ($\text{R} = \text{Ph}, \text{OMe}$), will catalyze carbodiimide metathesis and has proposed that the reactions involve intermediate metallocyclodiiminoimides formed by carbodiimide addition to the isonitrile complex.²⁸

Metallocycloacylthioamide Formation by Isothiocyanate Addition to 1. A surprising feature of the mechanism in Scheme V is that the first $\eta^1\text{-C}$ isothiocyanate complex ring closes through

Scheme V. Proposed Mechanism for the Formation of **5**

sulfur to give **6**, while the second ring closes through nitrogen to give **5**. This implies that metallocycle formation is either readily reversible, so that the outcome of the reaction is thermodynamically controlled by loss of gaseous COS, or that there is a fine kinetic balance in $\eta^1\text{-C}$ isothiocyanate complexes between ring closure through sulfur and ring closure through nitrogen. We cannot rule out the possibility that these reactions are reversible, but comparison of the reaction of $\text{S}=\text{C}=\text{NCH}_3$ with **1** with the reaction of $\text{S}=\text{C}=\text{NPh}$ with **1** suggests that there is indeed a fine balance between these competing modes of ring closure.

The reaction of $\text{S}=\text{C}=\text{NCH}_3$ with **1** was initially carried out by adding excess $\text{S}=\text{C}=\text{NCH}_3$ in THF to a dark green solution of **1** in diethyl ether at room temperature. This resulted in a slow color change to a cherry red solution, with concurrent deposition of a rust orange powder which could be recrystallized from THF/diethyl ether at low temperatures as red-orange flakes. Analysis and ^1H NMR established that these crystals were those of a monoisothiocyanate adduct of **1**, and comparison of the ^{13}C NMR spectrum of the complex with those of the previously characterized metalloheterocycles within this system (Table V) unambiguously established that the molecule contained an acyl group and a thioacyl group and that the adduct was therefore the metallocycloacylthioamide $[W(\eta\text{-C}_5\text{H}_5)_2[\text{C}(\text{S})\text{N}(\text{CH}_3)\text{C}(\text{O})]]$ (**8**). This could be formed as shown in Scheme VI by ring closure through nitrogen within an intermediate $\eta^1\text{-C}$ isothiocyanate complex.

The switch from a preference for initial ring closure through sulfur and ultimate formation of **5** in the $\text{S}=\text{C}=\text{NPh}$ reaction to initial ring closure through nitrogen and formation of **8** in the $\text{S}=\text{C}=\text{NMe}$ reaction can be rationalized in terms of an increase in the nucleophilicity of the nitrogen because of the methyl substituent. The ring closure mode is, however, finely balanced, and the ether supernatant contained small quantities of a second product which became a major product when the $\text{S}=\text{C}=\text{NCH}_3$ reaction was carried out in pentane instead of diethyl ether. Under these conditions the reaction yielded a mixture of two products—**8** (53%) and a second metalloheterocycle (27%) with a ^1H NMR spectrum containing a singlet cyclopentadienyl resonance at δ 4.98 and methyl resonances at δ 3.00 and 2.97. This suggested that the second material contained fragments derived from two isothiocyanate molecules, and examination of the ^{13}C NMR spectrum of the material in CD_2Cl_2 has led us to formulate the compound as $[W(\eta\text{-C}_5\text{H}_5)_2[\text{C}(\text{NCH}_3)\text{N}(\text{CH}_3)\text{C}(\text{S})]]$ (**9**) on the basis of the observation of resonances attributable to *N*-iminoacyl and a

(27) (a) Werner, H.; Heiser, B.; Burschka, C. *Chem. Ber.* **1982**, *115*, 3069.
(b) Werner, H. *Coord. Chem. Rev.* **1982**, *43*, 165.

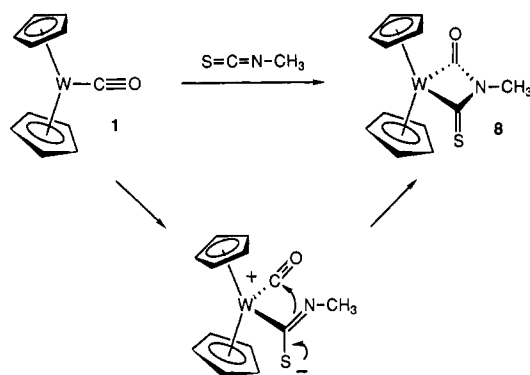
(28) Weiss, K.; Kindl, P. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 629.

Table VI. Bond Lengths (Å) within $[\text{W}(\eta\text{-C}_5\text{H}_5)_2[\text{C}(\text{S})\text{N}(\text{Ph})\text{C}(\text{NPh})]]^a$

W-C(1)	2.218 (11)	C(11)-C(12)	1.419 (17)	C(31)-C(32)	1.388 (16)
W-C(2)	2.184 (10)	C(12)-C(13)	1.414 (17)	C(32)-C(33)	1.368 (18)
W-C(11)	2.242 (11)	C(13)-C(14)	1.397 (19)	C(33)-C(34)	1.368 (20)
W-C(12)	2.271 (11)	C(14)-C(15)	1.399 (17)	C(34)-C(35)	1.375 (20)
W-C(13)	2.326 (11)	C(15)-C(11)	1.397 (19)	C(35)-C(36)	1.395 (17)
W-C(14)	2.364 (12)	C(21)-C(22)	1.444 (17)	C(36)-C(31)	1.403 (16)
W-C(15)	2.272 (12)	C(22)-C(23)	1.398 (18)	C(41)-C(42)	1.377 (15)
W-C(21)	2.250 (11)	C(23)-C(24)	1.401 (18)	C(42)-C(43)	1.394 (20)
W-C(22)	2.300 (10)	C(24)-C(25)	1.403 (18)	C(43)-C(44)	1.376 (22)
W-C(23)	2.353 (11)	C(25)-C(21)	1.422 (16)	C(44)-C(45)	1.351 (23)
W-C(24)	2.315 (12)			C(45)-C(46)	1.394 (19)
W-C(25)	2.242 (12)			C(46)-C(41)	1.355 (15)
C(1)-S(1)	1.612 (12)	C(1)-N(1)	1.393 (14)	C(2)-N(1)	1.416 (13)
C(2)-N(2)	1.282 (13)	N(2)-C(31)	1.387 (13)	N(1)-C(41)	1.443 (13)

^a See Figure 2 for atom designations.**Table VII.** Bond Angles (deg) within $[\text{W}(\eta\text{-C}_5\text{H}_5)_2[\text{C}(\text{S})\text{N}(\text{Ph})\text{C}(\text{NPh})]]^a$

C(1)-W-C(2)	61.9 (4)	C(11)-C(12)-C(13)	107.4 (11)	C(31)-C(32)-C(33)	122.8 (11)
W-C(1)-S(1)	139.4 (6)	C(12)-C(13)-C(14)	108.7 (10)	C(32)-C(33)-C(34)	120.3 (12)
W-C(2)-N(2)	144.9 (7)	C(13)-C(14)-C(15)	107.2 (12)	C(33)-C(34)-C(35)	119.4 (12)
W-C(1)-N(1)	95.0 (7)	C(14)-C(15)-C(11)	109.7 (12)	C(34)-C(35)-C(36)	120.3 (13)
W-C(2)-N(1)	95.7 (6)	C(15)-C(11)-C(12)	107.1 (11)	C(35)-C(36)-C(31)	121.0 (11)
C(1)-N(1)-C(2)	107.4 (8)	C(21)-C(22)-C(23)	107.8 (11)	C(36)-C(31)-C(32)	116.2 (10)
N(1)-C(1)-S(1)	125.6 (8)	C(22)-C(23)-C(24)	108.2 (11)	C(41)-C(42)-C(43)	118.4 (11)
N(2)-C(2)-N(1)	119.4 (9)	C(23)-C(24)-C(25)	109.4 (11)	C(42)-C(43)-C(44)	120.9 (13)
C(2)-N(1)-C(41)	125.7 (8)	C(24)-C(25)-C(21)	107.5 (11)	C(43)-C(44)-C(45)	119.6 (14)
C(1)-N(1)-C(41)	126.8 (9)	C(25)-C(21)-C(22)	107.0 (10)	C(44)-C(45)-C(46)	120.1 (13)
C(2)-N(2)-C(31)	118.4 (9)			C(45)-C(46)-C(41)	120.4 (12)
N(2)-C(31)-C(32)	121.7 (10)			C(46)-C(41)-C(42)	120.5 (11)
N(2)-C(31)-C(36)	121.6 (9)				
N(1)-C(41)-C(42)	118.3 (9)				
N(1)-C(41)-C(46)	120.9 (10)				

^a See Figure 2 for atom designations.**Scheme VI.** Proposed Mechanism for the Formation of **8**

thioacyl group (Table V). We have been unable to separate **9** from **8** and, hence, unable to definitely characterize **9**, but the similarity to **6** leaves little doubt that **9** is the double addition product, presumably formed by a mechanism similar to that in Scheme V.

Addition of Other Heteroallenes to 1. As previously reported¹⁰ we have been unable to form a metalloanhydride by addition of CO_2 to **1**, but most other heteroallenes react with **1**. In addition to those discussed above we have, for example, observed that **1** will react with CS_2 , COS, $\text{S}=\text{C}=\text{N}t\text{Bu}$, and $\text{O}=\text{C}=\text{CPh}_2$. None of these reactions gave tractable organometallic products, however, and they have not, therefore, been examined in detail.

Conclusion

It is clear from the results above that metallocyclohexene formation by addition of heteroallenes to carbonyl complexes is not limited to anionic carbonyl complexes, but that electron-rich neutral carbonyls can also participate in such reactions. In the specific case of $[\text{W}(\eta\text{-C}_5\text{H}_5)_2(\text{CO})]$, heteroallene addition provides access to a number of novel metallocyclohexenes of which the metallocycloimides **2** and **3** and the metallocycloacylthioamide **8** provide the first reported examples of these particular functional groups. These complexes will probably have a significant reaction chemistry, and efforts to develop this chemistry with the objective of discovering new approaches to the incorporation of heteroallene derived fragments into organic molecules are currently underway in our group.

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Supplementary Material Available: Tables of anisotropic temperature factors, calculated hydrogen parameters, least-squares planes, interplanar angles and angles about tungsten in **5** and a figure of packing within the unit cell for **5** (3 pages); table of observed and calculated structure factors for **5** (15 pages). Ordering information is given on any current masthead page.