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Registry No. GGG, 556-33-2; GGGa, 35790-47-7; AGG, 19729-30-7; GAG, 3146-40-5; GGA, 16422-05-2; Pd, 7440-05-3; Ni, 7440-02-0; Cu, 7440-50-8.

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Studies of the Reactions of Amines with Carbonyl Functions in Some Cyclopentadienyltungsten Carbonyl Complexes

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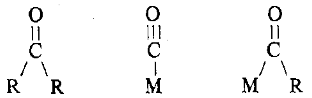
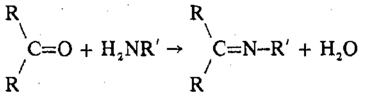
The compounds $(\eta^5\text{-}C_5H_5)W(CO)_3(CH_2COCH_3)$, I, and $(\eta^5\text{-}C_5H_5)W(CO)_3(COCH_3)$, II, have been investigated in their reactivity toward primary amines. I reacts with methylamine to form the compound $(\eta^5\text{-}C_5H_5)W(CO)_2(NH_2CH_3)(CONHCH_3)$, III, which was characterized by x-ray crystallographic methods. III crystallizes in the space group $P2_1/c$ [C_{2h}^5; No. 14]. At -26 °C, $a = 10.775$ (10), $b = 17.807$ (17), $c = 12.858$ (12) Å, $\beta = 97.27$ (3)°, $\rho_{calcd} = 2.14$ g cm^{-3}, $\rho_{obsd} = 2.13$ g cm^{-3} (at +20 °C), and $Z = 8$. III contains a normal η^5-cyclopentadienyl ring, two linear carbonyl groups, a coordinated methylamine ligand, and an *N*-methylcarbamoyl ligand. The metal-coordinated methylamine ligand is labile and is readily displaced by neutral donor ligands to form the new molecule $(\eta^5\text{-}C_5H_5)W(CO)_2L(CONHCH_3)$, where L = $CNCH_3$ and $P(C_6H_5)_3$. Complex II reacts with the primary amines RNH_2 (R = CH_3 and c-C_6H_{11}) to form $(\eta^5\text{-}C_5H_5)W(CO)_3H$ and the corresponding amide. The reactions of I evidently proceed smoothly through amine attack on the carbon monoxide ligands; however, the preferred site of attack in II appears to have shifted to the acetyl ligand.

Introduction

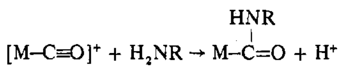
The carbonyl function is one of the most ubiquitous and chemically useful atomic groupings known to chemistry. In organic molecules it possesses the general form **1**, while in organometallic complexes it is represented by the linear end-on coordination of the carbon monoxide molecule, **2**. A combination of these two forms yields the organometallic acyl function, **3**.


1 2 3

A principal form of their reactivity is nucleophilic attack at the carbon atom. For example, primary amines readily attack organic ketones (**1**) to produce imines through the classic Shiff-base condensation reaction (1).[1] Metal carbonyls are also susceptible to nucleophilic attack by amines and produce metal carbamoyl complexes according to reaction 2.[2]



$$R_2C{=}O + H_2NR' \rightarrow R_2C{=}N{-}R' + H_2O \qquad (1)$$



$$[M{-}C{\equiv}O]^+ + H_2NR \rightarrow M{-}\overset{HNR}{\overset{|}{C}}{=}O + H^+ \qquad (2)$$

The reaction of the organometallic acyl function with amines has not been thoroughly investigated, although Heck has reported the formation of amides in the reaction of acyltetracarbonylcobalt compounds with nucleophilic amines.[3]

Studies of the reactivities of the various carbonyl functions as they occur in polyfunctional compounds have been wide and varied. For example, methoxide ion is known to react with acetylpentacarbonylmanganese through attack at the acyl carbon. This leads to formation of methyl acetate and pentacarbonylmanganate(I) anion.[4] On the other hand, methyllithium reacts with benzoylpentacarbonylmanganese through attack on a carbon atom of one of the cis-coordinated carbon monoxide ligands and produces *cis*-acetylbenzoyltetracarbonylmanganate(I) anion.[5] Theoretical considerations of coordinated carbon monoxide, acyl, and carbene functions have shown that the site of attack may be correlated with energy of the lowest unoccupied molecular orbital in the complex.[6] These calculations verified the high reactivity of the coordinated carbene but failed to provide a useful distinction between the acyl and carbon monoxide ligands.

Here, we wish to report the results of our studies of the reactions of primary amines with the carbonyl functions **1**–**3** as they occur in some cyclopentadienyltricarbonyltungsten complexes. This has been achieved by employing the complex $(\eta^5\text{-}C_5H_5)W(CO)_3(CH_2COCH_3)$, I, which contains both type **1** and **2** carbonyl functions and $(\eta^5\text{-}C_5H_5)W(CO)_3(COCH_3)$,

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II, which contains type **2** and **3** functions.

Experimental Section

General. All reactions were performed under an atmosphere of nitrogen. The solvents hexane, tetrahydrofuran, and toluene were dried by refluxing over sodium benzophenone and were distilled just prior to use. The amines and triphenylphosphine were obtained commercially and were used without further purification. (η^5-C_5H_5)W(CO)$_3$(CH_2COCH_3) was prepared as previously described.[7] (η^5-C_5H_5)W(CO)$_3$($COCH_3$) was prepared according to the method of Wilkinson for the preparation of (η^5-C_5H_5)W(CO)$_3$(COC_2H_5).[8] $CNCH_3$ was prepared by an established procedure.[9] Infrared spectra were recorded on a Perkin-Elmer 237 infrared spectrophotometer and were calibrated with polystyrene at 1601.4 cm^{-1}. Absorption positions are expected to be accurate to within ±3 cm^{-1}. ^{1}H NMR spectra were recorded on a Perkin-Elmer R-32 spectrometer operating in unlocked mode and calibrated with Me_4Si. Elemental microanalyses were performed by Midwest Microlab Ltd., Indianapolis, Ind.

Reaction of (η^5-C_5H_5)W(CO)$_3$(CH_2COCH_3) with CH_3NH_2. Preparation of (η^5-C_5H_5)W(CO)$_2$($CONHCH_3$)(NH_2CH_3), III. Approximately 1 mL of NH_2CH_3 was condensed in a Schwartz tube in liquid nitrogen. It was then allowed to warm and was distilled into a stirred solution of I (0.7 g, 1.80 mmol) in hexane (100 mL) at −78 °C. The cold bath was removed, and the solution was allowed to come slowly to room temperature. An insoluble oily orange precipitate formed on the sides of the flask. After being stirred at room temperature for 24 h, the yellow solution was decanted. The orange residue was washed with hexane, extracted with CH_2Cl_2, and filtered through a sintered-glass frit. The filtrate was concentrated in vacuo, and the addition of hexane at −78 °C produced orange crystals which were recrystallized from CH_2Cl_2/hexane at −78 °C. The yield was 0.45 g (64%); mp 100–105 °C dec; IR (CH_2Cl_2) 1906 (s), 1805 (s), 1600 (w) cm^{-1}; ^{1}H NMR (CD_2Cl_2) 5.37 (singlet, C_5H_5), 2.76 (doublet, J = 4.5 Hz, NHCH_3), 2.59 ppm (triplet, J = 6.3 Hz, $NH_2$$CH_3$). Anal. Calcd: C, 30.48; H, 3.58; N, 7.11. Found: C, 30.01, H, 3.58; N, 6.73.

(η^5-C_5H_5)W(CO)$_2$(P(C_6H_5)$_3$)($CONHCH_3$). A 0.295-g (0.75 mmol) amount of III and 0.195 g (0.75 mmol) of P(C_6H_5)$_3$ were combined in a three-necked flask, and $C_2H_4Cl_2$ (25 mL) was added at room temperature. The orange reaction mixture rapidly turned yellow and was allowed to stir for 75 min. The solvent was removed in vacuo, and the yellow residue crystallized from CH_2Cl_2/hexane at −78 °C, giving approximately 0.221 g of a yellow powder, which was washed with pentane and dried. The yield was 47%; mp 186 °C; IR (CH_2Cl_2) ν(CO) 1917 (w), 1835 (s), 1550 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$) 7.38 (multiplet, C_6H_5), 5.24 (doublet, $J_{P-H}{}^3$ = 3.0 Hz, C_5H_5), 2.72 ppm (doublet, J = 4.5 Hz, CH_3). Anal. Calcd: C, 51.86; H, 3.87; N, 2.24. Found: C, 51.11; H, 3.87; N, 2.13.

(η^5-C_5H_5)W(CO)$_2$($CNCH_3$)($CONHCH_3$). To a solution of 0.445 g (1.13 mmol) of III in THF (150 mL) was added 0.4 mL of $CNCH_3$ dropwise at room temperature. The clear orange solution rapidly became cloudy. After 6 h of stirring, the solvent was removed under reduced pressure. The residue was extracted with CH_2Cl_2, filtered through a sintered glass frit, and concentrated. Addition of pentane caused precipitation of a very fine light powder. The solution was then allowed to stand for 2 days at −20 °C. This produced a low yield of large light brown crystals, which were washed with hexane and dried. The yield was 10%; mp 164 °C dec; IR (THF) 1865 (s), 1935 (m), 2150 (w, broad), 1575 (w) cm^{-1}; ^{1}H NMR ($DCCl_3$) for a mixture of isomers: 5.38 (singlet, C_5H_5), 3.76 (singlet, CNCH_3), 2.75 (doublet, J = 5.4 Hz, NHCH_3), 5.55 (singlet, C_5H_5), 3.70 (singlet, CNCH_3), 2.72 ppm (doublet, J = 5.4 Hz, NHCH_3). Anal. Calcd: C, 32.70; H, 2.97; N, 6.93. Found: C, 31.84; H, 3.14; N, 6.84.

Reaction of (η^5-C_5H_5)W(CO)$_3$($COCH_3$), II, with CH_3NH_2. Approximately 2.5 mL of NH_2CH_3 was condensed into a Schwartz tube in liquid nitrogen. It was then allowed to warm and was distilled into a solution of I (0.36 g, 0.97 mmol) in hexane (120 mL) at −78 °C. The cold bath was removed, and the reaction mixture was allowed to warm slowly to room temperature. An orange oil formed in the flask. The solution was stirred for 21 h at room temperature and then refluxed for 5 h to ensure complete conversion. On cooling, a cream colored precipitate formed. The solvent was removed under reduced pressure. The residue was dissolved in benzene and chromatographed on Al_2O_3·6% H_2O. The benzene eluents were collected. The solvent was removed, and the residue sublimed for 4.5 h at 40 °C and 0.1 mmHg; 0.156 g of (η^5-C_5H_5)W(CO)$_3$H, 48.5% yield, was obtained. $CH_3CO(NHCH_3)$ eluted from the column with THF solvent. This was identified by IR and ^{1}H NMR through comparison with authentic material.

Table I. X-Ray Diffraction Data for (η^5-C_5H_5)W(CO)$_2$(NH_2CH_3)($CONHCH_3$)

(A) Crystal Data	
Space group	$P2_1/c$ [$C_{2h}{}^5$; No. 14]
Temperature	−26 °C
Cell parameters	a = 10.775 (10) A b = 17.807 (17) A c = 12.858 (12) A β = 97.27 (3)° V = 2447.2 A^3
Z	8
ρ_{calcd}	2.14 g cm^{-3}
ρ_{exptl}	2.13 g cm^{-3} (at +20 °C)
μ	99.97 cm^{-1}
(B) Intensity Measurement Data	
Radiation	Mo Kα
Monochromator	Graphite
Detector aperture	4 mm × 4 mm
Reflections measured	$+h$, $+k$, $+l$
Maximum 2θ	45°
Scan type	$\theta/2\theta$ moving crystal–moving counter
Scan speed	2.0° min^{-1}
Scan range	Kα_1 peak −0.6° to Kα_2 peak + 0.6°
Background	stationary counter–stationary crystal; 4.0 s at each end of scan
No. of data	3562
Data used, [$F^2 > 3\sigma(F^2)$]	2091

The reaction of II with c-$C_6H_{11}NH_2$ and workup were performed similarly.

Crystal and Molecular Structure of III. Crystals of III were obtained by cooling solutions in CH_2Cl_2/hexane, 1:4 v/v, to −20 °C. A thin plate was mounted in a glass capillary. Preliminary precession and Weissenberg photographs indicated monoclinic symmetry, and the systematic absences $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$, identified the space group as $P2_1/c$ [$C_{2h}{}^5$; No. 14]. A preliminary data set was collected at room temperature on a Picker FACS-1 automatic diffractometer; however, substantial crystal decomposition and a large absorption effect threatened the quality of the data in spite of routine corrections.

$\sigma(I)$ was determined from counting statistics employing a p-factor value of 0.04. The density was determined by flotation in a CCl_4/CH_3I solvent mixture, ρ_{obsd} = 2.13 g cm^{-3}, Z = 8, and two molecules are required in the asymmetric crystal unit. The structure was solved by Patterson and difference-Fourier methods.[10] Neutral atom-scattering factors were taken from the compilations of Cromer and Waber.[11] Anomalous dispersion corrections were made for the tungsten atoms.[12] Full-matrix least-squares refinement was used, and the function $\sum w_i(|F_o| - |F_c|)^2$ was minimized, where the weight, w_i, was taken as $4F_o{}^2/\sigma(F_o{}^2)$. Although ultimately it proved to be inadequate, this trial data set did allow the determination of all nonhydrogen atom positions. However, upon convergence the residuals

$$R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$$

$$R_w = (\Sigma w_i(|F_o| - |F_c|)^2/\Sigma w_i F_o{}^2)^{1/2}$$

were 0.113 and 0.142, respectively, and the molecular dimensions were fraught with unrealistic distortions. A second thicker crystal bounded by the faces {010}, {$1\bar{1}\bar{1}$}, {$11\bar{1}$}, (100), ($10\bar{4}$), (201), ($\bar{2}\bar{3}1$), and ($\bar{2}\bar{1}\bar{1}$), with approximate dimensions 0.17 × 0.14 × 0.08 mm, was selected and sealed in a glass capillary. It was then mounted approximately along the [619] direction on a goniometer head equipped with an Air Products Model AC-1-101A cryotip. A surrounding evacuated chamber was enclosed by a thin-walled beryllium shroud. Data were collected at −26 ± 2 °C. Unit cell parameters were determined at this temperature by the centering and least-squares refinement of 12 reflections in the 2θ range 20–28°. Crystal data and data collection parameters are listed in Table I. Of the 3562 reflections collected in the range 0° < 2θ < 45°, 2091 reflections were found to conform to the relation $F_o{}^2 > 3\sigma(F_o{}^2)$ after correction for Lorentz and po-

Table II. Atomic Coordinates for Crystalline $(\eta^5\text{-}C_5H_5)W(CO)_2(CON(H)CH_3)(NH_2CH_3)$

Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*
W1	0.33091 (11)	0.13181 (6)	0.37566 (9)	W2	−0.20214 (10)	0.06961 (7)	0.14845 (9)
O1	0.244 (2)	0.130 (1)	0.135 (2)	O2	0.825 (2)	0.096 (1)	0.389 (2)
O3	0.413 (3)	0.281 (2)	0.283 (2)	O4	0.811 (2)	0.238 (1)	0.201 (2)
O5	0.502 (2)	0.490 (1)	0.140 (1)	O6	0.947 (2)	0.485 (1)	0.332 (1)
N1	0.694 (2)	0.470 (1)	0.221 (2)	N2	0.075 (2)	0.439 (1)	0.225 (2)
N3	0.530 (2)	0.123 (1)	0.451 (2)	N4	0.948 (2)	0.094 (1)	0.039 (2)
C1	0.277 (2)	0.130 (2)	0.228 (2)	C2	0.816 (3)	0.085 (2)	0.300 (2)
C3	0.385 (3)	0.219 (2)	0.322 (3)	C4	0.808 (3)	0.172 (2)	0.174 (2)
C5	0.393 (3)	0.017 (2)	0.333 (2)	C6	0.054 (3)	0.491 (2)	0.303 (2)
C7	0.659 (3)	0.394 (2)	0.250 (2)	C8	0.989 (3)	0.378 (2)	0.185 (2)
C9	0.610 (3)	0.194 (2)	0.479 (3)	C10	0.965 (3)	0.331 (2)	0.496 (3)
CP11	0.235 (3)	0.302 (2)	0.001 (3)	CP21	0.679 (3)	0.176 (2)	−0.010 (2)
CP12	0.286 (3)	0.368 (2)	0.055 (2)	CP22	0.615 (3)	0.085 (2)	0.026 (2)
CP13	0.228 (3)	0.432 (3)	0.000 (3)	CP23	0.588 (2)	0.062 (2)	0.132 (2)
CP14	0.140 (3)	0.090 (2)	0.415 (2)	CP24	0.365 (3)	0.493 (2)	0.342 (2)
CP15	0.142 (3)	0.179 (2)	0.418 (3)	CP25	0.308 (3)	0.463 (2)	0.427 (3)

Table III. Thermal Parameters for Crystalline $(\eta^5\text{-}C_5H_5)W(CO)_2(CON(H)CH_3)(NH_2CH_3)$

Atom	B_{iso}	Atom	B_{iso}	Atom	B_{iso}	Atom	B_{iso}
O1	4.7 (6)	C7	3.5 (7)	O2	4.7 (5)	C8	3.5 (7)
O3	7.8 (8)	C9	4.5 (8)	O4	5.7 (6)	C10	4.6 (8)
O5	3.1 (4)	CP11	4.0 (7)	O6	2.5 (4)	CP21	3.4 (7)
N1	2.3 (5)	CP12	3.0 (6)	N2	3.0 (5)	CP22	3.7 (7)
N3	2.4 (5)	CP13	4.7 (8)	N4	3.3 (5)	CP23	2.2 (6)
C1	2.4 (6)	CP14	3.1 (7)	C2	3.1 (7)	CP24	3.8 (7)
C3	4.3 (8)	CP15	4.0 (7)	C4	4.0 (8)	CP25	4.1 (7)
C5	2.3 (6)			C6	2.5 (6)		

Atom	β_{11}[a,b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
W1	0.0530 (12)	0.0191 (4)	0.0255 (8)	0.0012 (7)	0.0056 (8)	0.0000 (5)
W2	0.0398 (12)	0.0207 (5)	0.0297 (9)	−0.0007 (7)	0.0078 (8)	−0.0028 (6)

[a] The form of the expression for the anisotropic temperature factors is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.
[b] Anisotropic temperature factors multiplied by 10.0.

Table IV. Bonded Intramolecular Distances for $(\eta^5\text{-}C_5H_5)W(CO)_2(CONHCH_3)(NH_2CH_3)$

Atoms	Distance, Å	Atoms	Distance, Å
W1–C1	1.91 (3)	W2–C2	1.95 (3)
W1–C3	1.83 (3)	W2–C4	1.86 (3)
W1–N3	2.24 (2)	W2–C6	2.16 (3)
W1–C5	2.25 (3)	W2–N4	2.31 (2)
W1–CP11	2.34 (3)	W2–CP21	2.45 (3)
W1–CP12	2.41 (3)	W2–CP22	2.38 (3)
W1–CP13	2.45 (3)	W2–CP23	2.25 (3)
W1–CP14	2.30 (3)	W2–CP24	2.24 (3)
W1–CP15	2.33 (3)	W2–CP25	2.36 (3)
C1–O1	1.21 (3)	C2–O2	1.15 (3)
C3–O3	1.26 (4)	C4–O4	1.21 (3)
C5–O5	1.25 (3)	C6–O6	1.25 (3)
C5–N1	1.37 (3)	C6–N2	1.41 (3)
N1–C7	1.48 (3)	N2–C8	1.48 (3)
N3–C9	1.56 (4)	N4–C10	1.48 (4)
CP11–CP12	1.42 (4)	CP21–CP22	1.44 (4)
CP11–CP15	1.41 (4)	CP21–CP25	1.48 (4)
CP12–CP13	1.45 (4)	CP22–CP23	1.49 (4)
CP13–CP14	1.40 (4)	CP23–CP24	1.35 (4)
CP14–CP15	1.58 (4)	CP24–CP25	1.41 (4)

Table V. Pertinent Intramolecular Angles for $(\eta^5\text{-}C_5H_5)W(CO)_2(CONHCH_3)(NH_2CH_3)$

Atoms	Angle, deg	Atoms	Angle, deg
C1–W1–C3	73 (1)	C2–W2–C4	72 (1)
C1–W1–N3	125 (1)	C2–W2–N4	126 (1)
C1–W1–C5	78 (1)	C2–W2–C6	80 (1)
C3–W1–N3	84 (1)	C4–W2–N4	84 (1)
C3–W1–C5	125 (1)	C4–W2–C6	124 (1)
N3–W1–C5	75 (1)	N4–W2–C6	75 (1)
W1–C1–O1	179 (3)	W2–C2–O2	178 (3)
W1–C3–O3	176 (3)	W2–C4–O4	173 (3)
W1–C5–O5	125 (2)	W2–C6–O6	130 (2)
W1–C5–N1	118 (2)	W2–C6–N2	117 (2)
O5–C5–N1	117 (2)	O6–C6–N2	113 (2)
C5–N1–C7	120 (2)	C6–N2–C8	125 (2)
W1–N3–C9	121 (2)	W2–N4–C10	122 (2)
CP15–CP11–CP12	116 (3)	CP25–CP21–CP22	108 (3)
CP11–CP12–CP13	107 (3)	CP21–CP22–CP23	102 (2)
CP12–CP13–CP14	111 (3)	CP22–CP23–CP24	112 (3)
CP13–CP14–CP15	105 (3)	CP23–CP24–CP25	110 (3)
CP14–CP15–CP11	105 (3)	CP24–CP25–CP21	108 (3)

larization effects. Three intense reflections were monitored frequently during the collection of the data and showed no evidence of crystal decomposition. A linear absorption correction was applied to the data using the Gaussian integration method with a grid of 10 × 4 × 10. The maximum and minimum transmission coefficients were 0.513 and 0.355, respectively.

The previously calculated positional and thermal parameters of the nonhydrogen atoms were used in the subsequent least-squares refinements. The metal atoms were refined with anisotropic temperature factors, while the remaining nonhydrogen atoms were refined with isotropic thermal parameters. Four cycles of full-matrix least-squares refinement reduced R and R_w to 0.062 and 0.070, respectively. During the final cycle of refinement, no parameter shifted by more than 0.36σ, where σ is the estimated standard deviation of that parameter. After the final cycle of refinement, the error in an observation of unit weight, $[\sum w_i(|F_o| - |F_c|)^2/(N_o - N_V)^{1/2}$, was 1.75. The quantity $w|F_o - F_c|^2$ was independent of both the magnitude of F_o and $\lambda^{-1} \sin \theta$. A final difference-Fourier synthesis was essentially featureless but showed numerous peaks in the vicinity of the tungsten atoms. The largest peak in the final difference-Fourier map was 2.35 e Å^{-3} near W2. Hydrogen atoms could not be found in this difference map, and no attempt to place them artificially was made. A final structure-factor calculation for all recorded reflections showed that the calculated structure factors for the rejected reflections were acceptably low.

Final atomic positional and thermal parameters are given in Tables II and III, respectively. Standard deviations were derived from the elements of the inverse matrix, obtained on the final cycle of least-squares refinement. Intramolecular bond distances and angles are listed in Tables IV and V. Tables of selected intermolecular bond

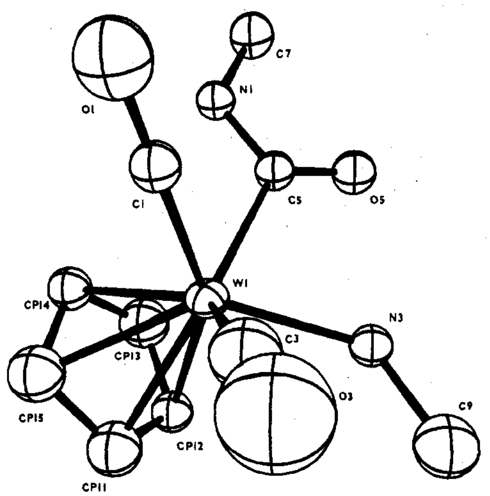

Figure 1. An ORTEP drawing of one of the two molecules of III in the crystallographic asymmetric unit. 50% probability ellipsoids are shown.

distances, various unit-weighted least-squares planes, observed and calculated structure-factor amplitudes, a molecular diagram of molecule **2**, and a crystal-packing diagram are available.[13]

Results

Reaction of (η^5-C_5H_5)W(CO)$_3$(CH_2COCH_3), I, with CH_3NH_2. The reaction of I with methylamine in hexane yielded an orange precipitate, III. Complex III readily decomposed in all common solvents; thus, most spectroscopic analyses were precluded or complicated due to the rapid formation of decomposition products. The complex was most stable in dried, degassed methylene chloride solvent, from which some crystals suitable for diffraction analysis were finally obtained. We have thus based our characterization of this complex on our crystal structure analysis, but this is also supported by IR and ^{1}H NMR spectroscopic analyses.

Compound III crystallizes in the centrosymmetric space group $P2_1/c$, $Z = 8$, and contains two crystallographically independent molecules in the asymmetric unit. The molecules are essentially identical structurally, and the molecular structure of one of these is shown in Figure 1. Pertinent intramolecular bond distances and angles are listed in Tables IV and V. Each molecule contains a η^5-cyclopentadienyl ring. The mean W–C(C_5H_5) and W–(ring plane) distances, ⟨2.36 (3)⟩ and ⟨1.99 (3) Å⟩, respectively, are similar to distances found in previously investigated (η^5-C_5H_5)W complexes: [(η^5-C_5H_5)W(CO)$_3$]$_2$,[14] ⟨2.34 (1)⟩ and ⟨2.01 (1) Å⟩; (η^5-C_5H_5)W(CO)$_3$AuP(C_6H_5)$_3$,[15] ⟨2.35 (7)⟩ and ⟨2.01 (6) Å⟩; [(η^5-C_5H_5)W(CO)$_3$]$_3$Ga,[16] ⟨2.343⟩ and ⟨2.01 Å⟩; (η^5-C_5H_5)W(CO$_3$Ga(CH_3)$_2$,[17] ⟨2.346⟩ and 2.00 Å; and [(η^5-C_5H_5)W(CO)$_3$Al(CH_3)$_2$]$_2$,[18] ⟨2.336⟩ and 2.016 Å. The mean C–C distance, ⟨1.44 (4) Å⟩, is also typical of distances found in other (η^5-C_5H_5)W complexes.[14–19] The cyclopentadienyl rings are essentially planar with no carbon atom deviating from the calculated mean plane by more than 0.023 Å.

Two cis-coordinated carbon monoxide ligands in each molecule are essentially linear. W–C–O angles range from 173 (3) to 179 (3)°, ⟨177 (3)°⟩. The range of these values is typical of terminally coordinated carbonyl ligands in organometallic complexes of tungsten, viz., [(η^5-C_5H_5)W(CO)$_3$]$_2$,[14] 173.2 (6)–178.2 (6)°, ⟨175.3 (6)°⟩; (η^5-C_5H_5)W(CO)$_3$AuP(C_6H_5)$_3$,[15] 168 (4)–177 (4)°; [(η^5-C_5H_5)W(CO)$_3$]$_3$Ga,[16] 173–177°, ⟨175°⟩; (η^5-C_5H_5)W(CO)$_3$Ga(CH_3)$_2$,[17] 172 (2)–176 (2)°, ⟨175°⟩; and (η^5-C_5H_5)W(CO)$_3$(C_6H_5),[19] 163–178°, ⟨169°⟩. The W–C and carbonyl C–O distances, ⟨1.89⟩ and ⟨1.21 Å⟩, are also similar to distances previously reported for tungsten carbonyl complexes.[14–19]

The two remaining ligands include: (1) an *N*-methylcarbamoyl group which was evidently formed by attack of a methylamine molecule on the third coordinated carbon monoxide ligand of the original tungsten complex, I. The identity of this group is supported by the observation of an infrared absorption at 1600 cm^{-1}, which is known to be characteristic of metal-coordinated carbamoyl ligands;[2] and (2) an *N*-coordinated methylamine ligand. The coordinated carbamoyl ligands including the atoms W1–C5–O5–N1–C7 (molecule **1**) and W2–C6–O6–N2–C8 (molecule **2**) are each planar with no atom deviating from the least-squares planes by more than 0.035 Å. The bond distances C5–O5 and C6–O6 both at 1.25 (3) Å and the distances C5–N1 = 1.37 (3) Å and C6–N2 = 1.41 (3) Å appear to be marginally longer than the corresponding distances found in organic amides.[20] The intramolecular angles O5–C5–N1 and O6–C6–N2 are 117 (2) and 113 (2)°, respectively. Overall, this ligand is remarkably similar to an identical *N*-methylcarbamoyl ligand that was structurally characterized in two different crystalline modifications of Mn(CO)$_4$(NH_2CH_3)($CONHCH_3$).[22] In these studies the ligand showed the distances C=O = 1.228 (10) and 1.251 (15) Å and C–N = 1.443 (27) and 1.345 (12) Å. The O–C–N angle was 116.7 (20) and 117.8 (8)°.

The tungsten–methylamino bond lengths, 2.24 (2) (W1) and 2.31 (2) Å (W2), are similar to the values reported for other nitrogen donor complexes of tungsten (W_2Cl_2(C_5H_5N)$_4$,[23] 2.24 (2) Å; (2,2′-bpy)(CO)$_2$BrWGeBr$_3$,[24] 2.21 (4) and 2.20 (4) Å), and, as expected, are considerably longer than the W–N distance reported for W(N(CH_3)$_2$)$_6$, ⟨2.032 (25) Å⟩,[25] for which partial multiple bonding between the tungsten and nitrogen atoms may be anticipated. The W–N–C angles are equal within their errors, ⟨121 (2)°⟩, and are identical with the angles reported for other methylamino–metal complexes: [Re(NH_2CH_3)$_4$(CH_3N)Cl]$^+$,[26] 121 (2)°; [Co(NH_2CH_3)$_5$Cl]$^{2+}$,[27] ⟨121.2 (4)°⟩; Mn(CO)$_4$(NH_2CH_3)($CONHCH_3$),[22] ⟨121.1 (7)°⟩ and 118.9 (10)°.

There are no abnormally short intermolecular contacts. The shortest distance is between carbamoyl oxygen and nitrogen atoms at 2.928 Å.

In further characterizations of III, we have investigated its reaction chemistry with neutral donor ligands. We have found that the methylamine ligand is readily displaced to give substitution products according to eq 3, for L = P(C_6H_5)$_3$ and

$$(\eta^5\text{-}C_5H_5)W(CO)_2(NH_2CH_3)(CONHCH_3) + L \rightarrow (\eta^5\text{-}C_5H_5)W(CO)_2(L)(CONHCH_3) + NH_2CH_3 \qquad (3)$$

$CNCH_3$. These complexes are considerably more stable than III and have been characterized by IR, ^{1}H NMR, and elemental analyses.

Reactions of (η^5-C_5H_5)W(CO)$_3$($COCH_3$), II, with Amines. The reactions of II with both methyl- and cyclohexylamine proceed according to eq 4 and produce good yields of (η^5-C_5H_5)W(CO)$_3$H and the corresponding amide.

$$(\eta^5\text{-}C_5H_5)W(CO)_3(COCH_3) + RNH_2 \rightarrow (\eta^5\text{-}C_5H_5)W(CO)_3H + CH_3CO(NHR) \qquad (4)$$

$$R = CH_3 \text{ and c-}C_6H_{11}$$

Discussion

As was pointed out in the Introduction, the carbon atoms of carbonyl functions are susceptible to nucleophilic attack. Compound I contains both type 1 and 2 carbonyl groups. We have found that I reacts with two molecules of methylamine to produce the carbamoyl complex III. We believe this occurs initially through attack of one methylamine molecule on a carbon atom of one of the coordinated carbon monoxide ligands, 2. This is followed by a proton transfer and elimination of the 2-oxoalkyl group, presumably as acetone.[28] A second molecule of methylamine then enters the coordination sphere of the tungsten atom in order to preserve its 18-electron configuration.

Complex II contains both type **2** and type **3** carbonyl functions. The reactions of II with primary amines invariably proceed to give $(\eta^5\text{-}C_5H_5)W(CO)_3H$ and amide. Unlike the reactions of I, the site of attack in II appears to have shifted from the carbon monoxide ligands to the carbon atom of the acetyl group. Subsequent proton transfer to the tungsten atom and cleavage of the metal acyl carbon bond result in formation of the tungsten hydride and the amide.

The reactions of I demonstrate the known reactivity of carbon monoxide ligands toward amines[2] but also indicate that they are more reactive than the organic carbonyl function, **1**, also present in this complex. The reactions of II indicate an even higher reactivity of the tungsten–acetyl group. While all the reactions evidently proceed via amine attack on the carbon atoms of the carbonyl functions, it is also clear that bond-making and -breaking processes about the tungsten atom must also play a key role in defining the ultimate reaction path. Presently, however, we are unable to ascertain the relative importance of these latter processes in determining the course of the reactions.

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Registry No. I, 60911-81-1; II, 64666-36-0; III, 64666-37-1; $(\eta^5\text{-}C_5H_5)W(CO)_2(P(C_6H_5)_3)(CONHCH_3)$, 64666-38-2; $(\eta^5\text{-}C_5H_5)W(CO)_2(CNCH_3)(CONHCH_3)$, 64666-39-3; $(\eta^5\text{-}C_5H_5)W(CO)_3H$, 12128-26-6; NH_2CH_3, 74-89-5.

Supplementary Material Available: Observed and calculated structure factor amplitudes, selected intermolecular bond distances, molecular diagram of molecule **2**, a crystal-packing diagram, and least-squares planes (18 pages). Ordering information is given on any current masthead page.

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Bidentate Chelate Compounds. 1. Pseudotetrahedral Copper(II) Complexes of Heterocyclic Secondary Amines

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Bis(heterocyclic secondary amine)copper(II) complexes of general formula $Cu(HL)_2(ClO_4)_2$, where HL = 2-pyridyl-2′-pyrimidylamine (HPPA), 2-pyridyl-2′-thiazolylamine (HPTA), 2-pyridyl-2′-(4′-methylthiazolyl)amine (HMPTA), and 2-(6-methylpyridyl)-2′-(4′-methylthiazolyl)amine (HDMPTA), have been prepared and characterized. Some of the complexes can be deprotonated to neutral complexes of general formula $M(L)_2$.[2] Spectral and magnetic data indicate a pseudotetrahedral geometry in the solid state for the copper(II) complexes; solution data indicate solvation of the protonated copper(II) complexes to species with coordination number six while the deprotonated complexes retain their coordination number of four. The d–d transitions in the solid-state spectra have been interpreted with the aid of an energy level diagram constructed for distortion of a tetrahedral CuN_4 chromophore and calibrated using the known spectrum of $Cu(HDPA)_2(ClO_4)_2$.

Introduction

The ability of 2,2′-dipyridylamine (HDPA) to coordinate as a bidentate ligand to transition metal cations, particularly to copper(II), has been extensively investigated.[3-6] The two ring nitrogen atoms act as the electron-pair donors in the majority of the compounds, although in some instances the bridging amine nitrogen appears to have donor properties.[7] A coordination number of four can be established when the ligand

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