Carboxamido Complexes of Molybdenum and Tungsten. Alkyl Isocyanate Insertion into a Tungsten–Hydrogen Bond

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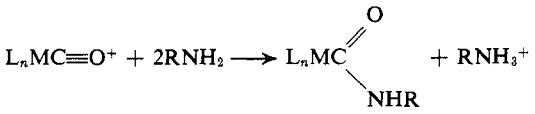
Abstract: The cationic complexes, $(C_5H_5)M(CO)_4{}^+$ (where M = Mo or W), react with secondary alkylamines (R_2NH) to form the carboxamido complexes $(C_5H_5)M(CO)_3C(O)NR_2$. Although analogous carboxamido derivatives are formed with limited amounts of primary amines, reaction with excess amine proceeds as follows: $(C_5H_5)M(CO)_4{}^+ + 4CH_3NH_2 \rightarrow (C_5H_5)M(CO)_3{}^- + 2CH_3NH_3{}^+ + (CH_3NH)_2CO$. That this reaction proceeds by initial formation of $(C_5H_5)M(CO)_3C(O)NHCH_3$ is strongly supported by the isolation of the tungsten complex which does react with excess amine to give the urea and other products noted in the above equation. This reaction apparently occurs by initial removal of the carboxamido NH proton by the amine leaving a complex which decomposes to methyl isocyanate. The isocyanate then rapidly reacts with additional amine to give the observed urea. The intermediacy of CH_3NCO is strongly supported by the reaction of the carboxamido complex with Et_3N: $(C_5H_5)W(CO)_3C(O)NHCH_3 + Et_3N \rightleftarrows Et_3NH^+ + (C_5H_5)W(CO)_3{}^- + CH_3NCO$. This is an equilibrium which can be established by starting with reactants from either side of the equation. Building on this equilibrium, CH_3NCO has been inserted into the W–H bond to yield the carboxamido derivative, $(C_5H_5)W(CO)_3H + CH_3NCO \rightarrow (C_5H_5)W(CO)_3C(O)NHCH_3$, using Et_3N as the catalyst.

Recently we have demonstrated that with few exceptions cationic metal carbonyl complexes react with primary and secondary alkylamines to form carboxamido complexes according to eq 1. Such re-



$$L_nMC{\equiv}O^+ + 2RNH_2 \longrightarrow L_nMC(=O)NHR + RNH_3{}^+ \quad (1)$$

actions have been found for complexes of Ru,[2] Re,[3] Fe,[4,5] Mn,[6] Pt,[7] and Pd.[7] In the present paper, we report the synthesis of Mo and W carboxamido complexes by this route. The tungsten complex may also be prepared by the novel insertion of methyl isocyanate into a W–H bond. In the presence of excess alkylamine, the secondary carboxamido complexes react to yield 1,3-dialkylureas. The mechanism of this reaction is examined in some detail.

Results and Discussion

Preparation of Carboxamido Complexes. The cationic complexes, $[(C_5H_5)W(CO)_4]PF_6$ and $[(C_5H_5)Mo(CO)_4]PF_6$, react at room temperature with excess secondary alkylamines to form carboxamido complexes according to eq 2. The most stable products were

$$(C_5H_5)M(CO)_4{}^+ + 2R_2NH \longrightarrow (C_5H_5)M(CO)_3(CONR_2) + R_2NH_2{}^+ \quad (2)$$
$$M = \text{Mo or W}$$

isolated with $(CH_3)_2NH$ and piperidine. The derivatives of tungsten, which were more stable than those of molybdenum, were moderately air-stable in the crystalline state. Yet their syntheses had to be carried out with the rigorous exclusion of air to avoid decomposition to the $[(C_5H_5)W(CO)_3]_2$ dimer.

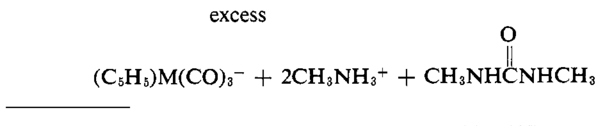
Their infrared spectra (Table I) showed two strong C–O stretching absorptions at approximately 2018 and 1933 cm^{-1}; the lower frequency absorption exhibited a shoulder. The room temperature proton nmr spectra (Table I) of the $(C_5H_5)M(CO)_3CON(CH_3)_2$ derivatives showed sharp singlets for the C_5H_5 and CH_3 protons. On cooling to −30°, the CH_3 resonance of the tungsten complex split into two lines indicating the nonequivalence of the two methyl groups presumably caused by restricted rotation around the C–N bond of the carboxamido group. Such restricted rotation in organic amides has been studied extensively.[8]

Primary amines also react with the cationic carbonyls to give carboxamido complexes.

$$(C_5H_5)M(CO)_4{}^+ + 2RNH_2 \longrightarrow (C_5H_5)M(CO)_3(CONHR) + RNH_3{}^+ \quad (3)$$

It is especially important that no more than 2 mol equiv of the amine be used to avoid formation of the 1,3-dialkylurea and $(C_5H_5)W(CO)_3{}^-$ (see below). The carboxamido complexes of tungsten where R = CH_3 and $-C(CH_3)_3$ have been isolated and analyzed. The molybdenum analogs readily decomposed to $[(C_5H_5)Mo(CO)_3]_2$ and were too unstable to isolate in pure form. Their presence was established by the similarity of their C–O stretching spectra (Table I) to those of the W analogs and also to those of the tertiary carboxamido complexes of molybdenum discussed above. The proton nmr spectrum of $(C_5H_5)W(CO)_3CONHCH_3$ showed a singlet for the cyclopentadienyl group and a doublet (J_{HCNH} = 5 Hz) for the CH_3 protons. The N–H proton was located as a broad singlet at approximately τ 4.0.

Excess CH_3NH_2 with $(C_5H_5)M(CO)_4{}^+$. With excess primary amine, the reaction proceeded as follows.



$$(C_5H_5)M(CO)_4{}^+ + \underset{\text{excess}}{4CH_3NH_2} \longrightarrow (C_5H_5)M(CO)_3{}^- + 2CH_3NH_3{}^+ + CH_3NHC(=O)NHCH_3 \quad (4)$$

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[1] Fellow of The Alfred P. Sloan Foundation, 1970–1972.

[2] A. E. Kruse and R. J. Angelici, *J. Organometal. Chem.*, **24**, 231 (1970).

[3] R. J. Angelici and A. E. Kruse, *ibid.*, **22**, 461 (1970).

[4] R. J. Angelici and L. Busetto, *J. Amer. Chem. Soc.*, **91**, 3197 (1969).

[5] L. Busetto and R. J. Angelici, *Inorg. Chim. Acta*, **2**, 391 (1968).

[6] R. J. Angelici and D. L. Denton, *ibid.*, **2**, 3 (1968).

[7] C. R. Green and R. J. Angelici, *Inorg. Chem.*, submitted for publication.

[8] H. Kessler, *Angew. Chem., Int. Ed. Engl.*, **9**, 219 (1970).

Table I. Infrared and ^{1}H Nmr Data

	Solvent	ν(CO), cm^{-1}	^{1}H nmr, τ: C_5H_5	^{1}H nmr, τ: CH_3
$C_5H_5W(CO)_3CONHCH_3$[a]	CCl_4	2018 s, 1928 vs, 1597 m	4.20[b]	7.38[b,c]
$C_5H_5W(CO)_3CONHC(CH_3)_3$	Hexane	2016 s, 1930 vs, 1627 m		
$C_5H_5W(CO)_3CON(CH_3)_2$	Hexane	2016 s, 1928 vs, 1576 m	4.17[b]	7.16[b]
$C_5H_5W(CO)_3CON(CH_2)_5$	Heptane	2015 s, 1930 vs, 1926 ssh, 1571 m		
$C_5H_5Mo(CO)_3CONHCH_3$[d]	CCl_4	2020 s, 1935 vs, 1614 m		
$C_5H_5Mo(CO)_3CON(CH_3)_2$	Hexane	2019 s, 1941 vs, 1934 s, 1594 m	4.37[b]	7.40[b]
$C_5H_5Mo(CO)_3CON(CH_2)_5$	Heptane	2018 s, 1937 vs, 1931 ssh, 1590 m		
$C_5H_5W(CO)_3H$	Hexane	2027 s, 1938 vs	4.50[e,f]	
	THF	2016 s, 1922 vs		
$C_5H_5W(CO)_3^-Na^+$	THF	1890 s, 1790 vs, 1739 s	4.98[e]	
$C_5H_5W(CO)_4^+PF_6^-$	CH_2Cl_2	2118 m, 2034 sh, 2010 s	3.90[e]	

[a] Nmr in CD_3CN–C_5H_5, τ 4.40; CH_3, τ 7.49; NH, τ 4.0 broad. [b] In acetone-d_6 solvent at ambient temperature. [c] J_{HCNH} = 5 Hz. [d] Additional weak bonds observed at 2056, 1985, and 1959 cm^{-1}. [e] In acetonitrile-d_3 solvent at ambient temperature. [f] W–H at τ 17.27.

The infrared spectra of these reaction mixtures exhibited strong C–O stretching absorptions at approximately 1890 and 1770 cm^{-1} for both Mo and W; these are characteristic of the $(C_5H_5)M(CO)_3^-$ anions. It should be noted that these frequencies differ slightly from that of an authentic sample of $(C_5H_5)W(CO)_3^-Na^+$ in tetrahydrofuran (THF) solution (Table I), which gives three absorptions. However, on addition of excess CH_3NH_2 the spectrum of $(C_5H_5)W(CO)_3^-Na^+$ changes to that observed in the reaction mixtures; *i.e.*, the spectrum of the anion is quite solvent dependent.

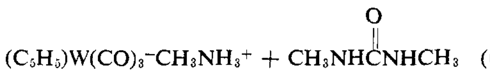
On evaporating the reaction solution, $(C_5H_5)W(CO)_3H$ and $(C_5H_5)Mo(CO)_3H$ could be sublimed, suggesting that $[(C_5H_5)M(CO)_3^-][CH_3NH_3^+]$ decomposed under the sublimation conditions to yield $(C_5H_5)M(CO)_3H$ and CH_3NH_2. This was verified for tungsten by first preparing the salt from the reaction of $(C_5H_5)W(CO)_3H$[9] with excess amine in THF.

$$(C_5H_5)W(CO)_3H + CH_3NH_2 \underset{\Delta}{\rightleftharpoons} [(C_5H_5)W(CO)_3^-][CH_3NH_3^+] \quad (5)$$

The presence of the anion in the salt was verified by infrared and by reaction with $(C_6H_5)_3GeBr$ to form $(C_5H_5)W(CO)_3Ge(C_6H_5)_3$[10] in 81% yield. On heating the solid $[(C_5H_5)W(CO)_3^-][CH_3NH_3^+]$ under high vacuum in a sublimation apparatus at 60°, 89% of the calculated amount from the reverse of eq 5 of $(C_5H_5)W(CO)_3H$ sublimed and 90% of the liberated CH_3NH_2 was trapped at −196°. Since the infrared spectrum of $(C_5H_5)W(CO)_3H$ is very similar to that of $(C_5H_5)W(CO)_3CONHCH_3$ (Table I), the presence of the hydride complex was further confirmed by reacting the sublimate with CCl_4 to give $(C_5H_5)W(CO)_3Cl$, a well-known reaction.[9]

The 1,3-dimethylurea produced in reaction 4 was sublimed and identified by its infrared and nmr spectrum; a known sample of the urea was prepared from CH_3NCO and CH_3NH_2. Products of reaction 4, where M = Mo, were characterized in the same manner.

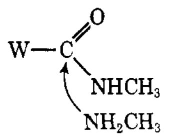
Since the carboxamido complexes, $(C_5H_5)M(CO)_3CONHCH_3$, were obtained in the presence of smaller amounts of CH_3NH_2, it was felt that reaction 4 proceeds by a mechanism involving initial formation of $(C_5H_5)M(CO)_3CONHCH_3$ followed by reaction with additional amine to give the observed products. That this is true was established for the relatively stable tungsten carboxamido complex by carrying out the reaction



$$(C_5H_5)W(CO)_3CONHCH_3 + \underset{\text{excess}}{2CH_3NH_2} \longrightarrow (C_5H_5)W(CO)_3^-CH_3NH_3^+ + CH_3NH\overset{O}{\overset{\|}{C}}NHCH_3 \quad (6)$$

When conducted in THF solvent at room temperature in an nmr tube using 3 mol of amine per mole of complex, only the products of reaction 6 were observed. This was indicated by resonances at τ 5.10 (singlet for C_5H_5 of $C_5H_5W(CO)_3^-$), 7.44 (broad for CH_3 of $(CH_3NH)_2CO$),[11] 7.60 (singlet for CH_3 of the CH_3NH_2–$CH_3NH_3^+$ mixture), and 4.6 (broad for all NH protons); these assignments were made on the basis of spectra of known samples of each of the species. The occurrence of reaction 6 is strong evidence that reaction 4 does involve initial formation of the carboxamido complex.

It is of interest to consider the mechanism of reaction 6. Of the two likely pathways, one involves direct attack of the amine on the carboxamido carbon



to yield the urea directly after loss of a proton. Such a mechanism has been previously postulated[12] for the reaction of $Mn(CO)_6^+$ with NH_3 to yield urea, NH_4^+, and $Mn(CO)_5^-$, although a carboxamido complex was not established as an intermediate in that reaction.

The other mechanism is one in which the amine acts first as a base to remove the NH proton from the carboxamido group leaving an anion which rapidly dissociates to $(C_5H_5)W(CO)_3^-$ and CH_3NCO. The CH_3NCO then rapidly reacts with excess amine to give the urea. This is summarized in eq 7. There is no precedent for this type of reaction in carboxamido complex chemistry and even organic amides require

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[9] T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956); E. O. Fischer, W. Hafner, and H. O. Stahl, *Z. Anorg. Allg. Chem.*, **282**, 47 (1955).

[10] H. R. H. Patel and W. A. G. Graham, *Inorg. Chem.*, **5**, 1401 (1966).

[11] This resonance splits into a doublet (J_{HCNH} = 5 Hz) in the presence of additional CH_3NH_2.

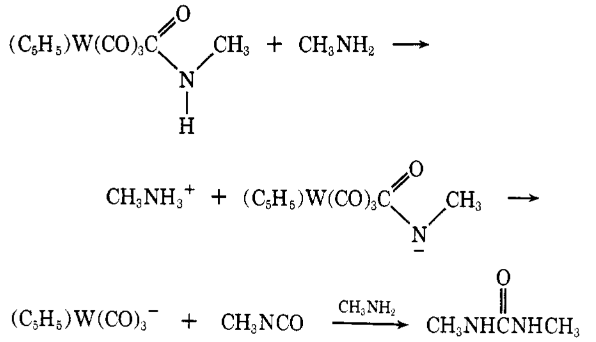
[12] H. Behrens, E. Ruyter, and H. Wakamatsu, *Z. Anorg. Allg. Chem.*, **349**, 241 (1967).

Table II. ^1H Nmr Spectra of Reaction 8 in CD_3CN

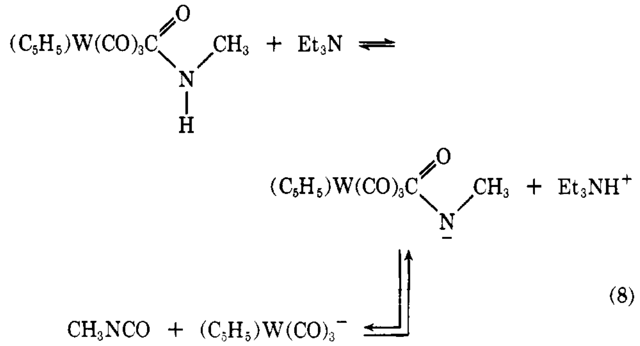
	Assignment	τ	$(C_5H_5)W(CO)_3C(O)NHCH_3$[a] + $(C_2H_5)_3N$[b] Rel intensity	$(C_5H_5)W(CO)_3H$[c] + CH_3NCO[d] + $(C_2H_5)_3N$[e] Rel intensity
$C_5H_5W(CO)_3C(O)NHCH_3$	C_5H_5	4.41	1.45	1.40
	CH_3	7.50[f]	0.87	0.84
$C_5H_5W(CO)_3^-$	C_5H_5	4.98	5.05	3.80
CH_3NCO	CH_3	7.07	3.30	5.80
$(C_2H_5)_3N$-$(C_2H_5)_3NH^+$[g]	CH_3	8.85	11.60	11.30[h]
	CH_2	7.07	7.74	7.55[i]
	NH	3.21	0.97	0.70[j]

[a] 0.274 mmol. [b] 0.272 mmol. [c] 0.339 mmol. [d] 0.657 mmol. [e] 0.408 mmol. [f] J_{HCNH} = 4.5 Hz. [g] For $(C_2H_5)_3N$ in CD_3CN, CH_3 (τ 9.07, J_{HCCH} = 7.0 Hz) and CH_2 (τ 7.62, J_{HCCH} = 7.0). [h] At τ 8.90, J_{HCCH} = 7.0 Hz. [i] At τ 7.17, J_{HCCH} = 7.0. [j] At τ 3.03.

considerably stronger bases than amines to remove an amide NH proton. But if mechanism 7 did operate it should be possible to use a tertiary amine (*e.g.*, Et_3N) which would act as the base in the first step but could not react with the resulting CH_3NCO to give a urea; hence the reaction should stop at the formation of the CH_3NCO.



(7)



(8)

This reaction was carried out in a sealed nmr tube using 0.111 g (0.274 mmol) of $(C_5H_5)W(CO)_3C(O)NHCH_3$ and 0.0274 g (0.272 mmol) of Et_3N in approximately 0.4 ml of CD_3CN. The room temperature proton nmr spectrum was recorded as soon as possible after mixing and it did not change on standing for several hours. It showed the resonances with their relative intensities that are given in Table II. These data show that an equilibrium mixture of all of the species given in eq 8 (except the postulated intermediate $(C_5H_5)W(CO)_3C(O)NCH_3^-$ for which there is no evidence) are present in solution and that only 22% of the original $(C_5H_5)W(CO)_3C(O)NHCH_3$ remains while 78% is converted to $(C_5H_5)W(CO)_3^-$. The proton nmr assignments were all confirmed using authentic samples of the species. Moreover, the volatile species, CH_3NCO and $(C_2H_5)_3N$, were further established by vacuum distillation to another nmr sample tube where their spectra were also recorded. The formation of CH_3NCO by this reaction thus strongly supports the functioning of mechanism 7 in the conversion of the carboxamido complex to the urea (eq 6).

Since reaction 8 was rapid and stopped at an equilibrium mixture of reactants and products, it seemed that the same mixture could be obtained by starting with the products, CH_3NCO, $(C_5H_5)W(CO)_3^-$, and Et_3NH^+. The latter two are quantitatively produced in the equimolar reaction of $(C_5H_5)W(CO)_3H$ and Et_3N. Thus the nmr spectrum of 0.113 g (0.339 mmol) of $(C_5H_5)W(CO)_3H$, 0.0410 g (0.408 mmol) of Et_3N, and 0.0374 g (0.657 mmol) of CH_3NCO in approximately 0.4 ml of CD_3CN was obtained and found (Table II) to contain the same equilibrium mixture. Under these conditions, 27% of the tungsten existed in the carboxamido form while 73% was present as $(C_5H_5)W(CO)_3$.

An attempt to carry out the reverse of reaction 8 by mixing $(C_5H_5)W(CO)_3^-Na^+$, CH_3NCO, and acetic acid yielded only $(C_5H_5)W(CO)_3H$. This reaction was also complicated by the presence of impurities in the $(C_5H_5)W(CO)_3^-Na^+$ which catalyzed the polymerization of CH_3NCO. Even in the absence of these impurities, the carboxamido complex was not obtained.

On the basis of these studies, we conclude that the reaction of $(C_5H_5)W(CO)_4^+$ with CH_3NH_2 according to eq 4 proceeds by initial formation of the carboxamido complex (eq 3), followed by reaction (eq 7) with excess amine to generate CH_3NCO as an intermediate which with additional amine rapidly yields 1,3-dimethylurea.

To determine whether other carboxamido complexes could be deprotonated either by Et_3N or CH_3NH_2, we carried out the same nmr studies on $(C_5H_5)Fe(CO)_2C(O)NHCH_3$.[5] In this case, there was no reaction with either amine suggesting that the proton is less acidic than in $(C_5H_5)W(CO)_3C(O)NHCH_3$. This is consistent with the higher basicity[13] of $(C_5H_5)Fe(CO)_2^-$ as compared to $(C_5H_5)W(CO)_3^-$.

CH_3NCO Insertion into the W–H Bond. The rapid attainment of equilibrium in reaction 8 suggested that $(C_5H_5)W(CO)_3H$, in the presence of a small amount of Et_3N to generate $(C_5H_5)W(CO)_3^-$, should react with CH_3NCO to give the carboxamido complex

$$(C_5H_5)W(CO)_3H + CH_3NCO \overset{Et_3N}{\rightleftharpoons} (C_5H_5)W(CO)_3C(O)NHCH_3 \quad (9)$$

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(13) D. F. Shriver, *Accounts Chem. Res.*, **3**, 231 (1970).

This reaction has been carried out on a preparative scale using an excess of CH_3NCO to drive the equilibrium to the right. Although the reaction formally appears to be an insertion of CH_3NCO into the W–H bond, mechanistically it almost certainly proceeds by nucleophilic attack of $(C_5H_5)W(CO)_3^-$ on the isocyanate (reverse of eq 8). No reaction occurred between $(C_5H_5)W(CO)_3H$ and CH_3NCO in the absence of Et_3N.

Experimental Section

Materials. Methyl isccyanate was prepared[14] from acetyl chloride and sodium azide in 2,2′-diethoxydiethyl ether (bp 189°) solvent. The metal complexes $(C_5H_5)W(CO)_3Cl$, $(C_5H_5)Mo(CO)_3Cl$, and $(C_5H_5)W(CO)_3H$ were synthesized according to literature procedures.[9] The $[(C_5H_5)W(CO)_4]PF_6$ and $[(C_5H_5)Mo(CO)_4]PF_6$ were prepared from 2.75 mmol of $(C_5H_5)M(CO)_3Cl$ and 37.5 mmol of $AlCl_3$ in 35 ml of dry benzene under a CO pressure of 1500 psi at 45° for 6 days. The pressure and temperature used were considerably less than reported in the original syntheses[15] of these compounds. All reactions were carried out under a nitrogen atmosphere in oxygen-free solvents dried over CaH_2 or $LiAlH_4$.

$(C_5H_5)W(CO)_3C(O)N(CH_3)_2$. On a vacuum line, 50 ml of diethyl ether and 3.0 ml of $(CH_3)_2NH$ were distilled onto a sample of 1.42 g of $[(C_5H_5)W(CO)_4]PF_6$ at −196°. The mixture was allowed to warm to room temperature and was stirred for 20 min. The solution was evaporated to dryness under vacuum, leaving a yellow crystalline solid. The solid was extracted with warm pentane; on cooling the solution to 0° yellow analytically pure crystals of $(C_5H_5)W(CO)_3C(O)N(CH_3)_2$ precipitated. Additional pentane extractions gave an almost quantitative yield of the product, mp 117–119°.

Anal. Calcd for $(C_5H_5)W(CO)_3C(O)N(CH_3)_2$: C, 32.62; H, 2.74; N, 3.46. Found: C, 33.06; H, 3.16; N, 3.42.

$(C_5H_5)W(CO)_3C(O)N(CH_2)_5$. In 100 ml of diethyl ether, 1.9 g (3.7 mmol) of $[(C_5H_5)W(CO)_4]PF_6$ was treated with 5.0 ml (51 mmol) of piperidine at −196°. After stirring at room temperature for 30 min, the yellow solution was decanted from the solid. On cooling at −78° overnight, the yellow analytically pure product (mp 110° dec) precipitated from solution.

Anal. Calcd for $(C_5H_5)W(CO)_3C(O)N(CH_2)_5$: C, 37.78; H, 3.40; N, 3.15. Found: C, 37.76; H, 3.60; N, 3.28.

$(C_5H_5)Mo(CO)_3C(O)N(CH_2)_5$. In 50 ml of diethyl ether, 1.37 g (3.28 mmol) of $[(C_5H_5)Mo(CO)_4]PF_6$ was allowed to react with 0.294 g (6.54 mmol) of $(CH_3)_2NH$. The solution turned from colorless to orange-yellow and was then decanted from the solid. On cooling to −78°, orange-yellow crystals (0.11 g) of the product (mp 70° dec) precipitated.

Anal. Calcd for $(C_5H_5)Mo(CO)_3C(O)N(CH_3)_2$: C, 41.66; H, 3.50; N, 4.42. Found: C, 43.14; H, 3.66; N, 4.47.

$(C_5H_5)Mo(CO)_3C(O)N(CH_2)_5$. On a vacuum line, 5.5 ml of piperidine was distilled into a Schlenk tube containing 3.12 g (7.47 mmol) of $[(C_5H_5)Mo(CO)_4]PF_6$ in 100 ml of ether. After stirring for 30 min at room temperature, the solution was decanted from the solid and cooled at −78° overnight. The resulting coarse yellow crystals were filtered and dried under vacuum to give the pure product (mp 70° dec).

Anal. Calcd for $(C_5H_5)Mo(CO)_3C(O)N(CH_2)_5$: C, 47.07; H, 4.23; N, 3.92. Found: C, 47.18; H, 4.31; N, 3.88.

$(C_5H_5)W(CO)_3C(O)NHCH_3$. In a suspension of 4.0 g (7.9 mmol) of $[(C_5H_5)W(CO)_4]PF_6$ in 80 ml of ether at −196° was distilled 0.49 g (15.9 mmol) of CH_3NH_2. After warming to room temperature, the solution was stirred for 12 hr. An additional 60 ml of ether was distilled into the mixture which was then warmed to near the boiling point of the solvent. The solution was filtered and cooled to 0° overnight. Yellow needles of the pure product (mp 122–124°) were filtered and dried under vacuum.

Anal. Calcd for $(C_5H_5)W(CO)_3C(O)NHCH_3$: C, 30.72; H, 2.32; N, 3.58. Found: C, 31.25; H, 2.40; N, 3.46.

$(C_5H_5)W(CO)_3C(O)NHC(CH_3)_3$. A mixture of 1.52 g (3.0 mmol) of $[(C_5H_5)W(CO)_4]PF_6$ and 0.53 g (7.3 mmol) of $(CH_3)_3CNH_2$ in 45 ml of THF was stirred for 1 hr at room temperature. The deep orange solution was evaporated to dryness leaving a pink powder which was extracted with warm pentane. On slowly cooling the pentane extract to −78°, the powdery product, approximately 35% yield, precipitated. Even in the solid state, it slowly decomposes to $[(C_5H_5)W(CO)_3]_2$.

Anal. Calcd for $(C_5H_5)W(CO)_3C(O)NHC(CH_3)_3$: C, 36.05; H, 3.49; N, 3.23. Found: C, 35.41; H, 3.62; N, 3.14.

Although the analogous $(C_5H_5)Mo(CO)_3C(O)NHCH_3$ could be prepared and isolated similarly, its rapid decomposition to $[C_5H_5Mo(CO)_3]_2$ prevented its characterization by elemental analysis.

Reaction of $[(C_5H_5)W(CO)_4]PF_6$ with Excess CH_3NH_2. Ether (60 ml) and 10 ml of CH_3NH_2 were successively condensed into a Schlenk tube containing 3.12 g (6.18 mmol) of $[(C_5H_5)W(CO)_4]PF_6$ at −196°. After warming to room temperature, the mixture was stirred for 1 hr during which time the solution turned yellow and a yellow oil separated. The ether and excess amine were removed under vacuum and after an additional 2 hr under vacuum the yellow oil solidified. Sublimation of this solid at 50° under vacuum onto a water-cooled probe initially produced pale yellow $(C_5H_5)W(CO)_3H$ followed by white $(CH_3NH)_2CO$ needles over a total period of 3 days. (The combined yield was 2.25 g, which compares with 100% yields of 2.06 g for $(C_5H_5)W(CO)_3H$ and 0.54 g of $(CH_3NH)_2CO$.) During the sublimination gaseous CH_3NH_2 was evolved and trapped at −196°. The amine was allowed to react with excess $(CH_3)_3CNCO$ in pentane to give a white flaky precipitate of the methyl-*tert*-butylurea, $CH_3NHC(O)NHC(CH_3)_3$, which was identified by comparing its ir and nmr spectra with an authentic sample prepared by the reaction of CH_3NH_2 and $(CH_3)_3CNCO$.

The sublimed mixture was then treated with CCl_4 to convert the hydride to the chloride complex according to the well-known reaction[9]

$$(C_5H_5)W(CO)_3H + CCl_4 \longrightarrow (C_5H_5)W(CO)_3Cl + CHCl_3$$

After removal of the CCl_4, the residue was extracted with three 10-ml aliquots of water. The water extract was evaporated to dryness, and the solid was sublimed at 60° to give 0.35 g (65% yield) of $(CH_3NH)_2CO$, which was identified by comparing its ir and nmr spectra with an authentic sample. The water-insoluble material from the water extraction was dried under vacuum and consisted of 1.87 g (5.08 mmol, 82%) of $(C_5H_5)W(CO)_3Cl$, as identified by its C–O stretching absorptions at 2051 (m), 1971 (vs), and 1951 (s) cm^{-1} in hexane solvent.

The residue (1.32 g) from the initial sublimation was washed with several aliquots of water to remove $[CH_3NH_3]PF_6$, leaving 0.13 g (0.195 mmol) of $[(C_5H_5)W(CO)_3]_2$ identified by its ir spectrum in CH_2Cl_2 solvent showing absorptions at 1954 (vs) and 1903 (s, br) cm^{-1}. This small amount of $[(C_5H_5)W(CO)_3]_2$ presumably resulted from some decomposition of $(C_5H_5)W(CO)_3H$.[9]

Reaction of $[(C_5H_5)Mo(CO)_4]PF_6$ with Excess CH_3NH_2. The reaction of 2.34 g (5.60 mmol) of $[(C_5H_5)Mo(CO)_4]PF_6$ with 9.0 ml of CH_3NH_2 in 60 ml of ether was carried out and worked up in the same way as for the tungsten complex. The isolated products were 0.184 g (2.09 mmol, 37%) of $(CH_3NH)_2CO$, 0.73 g (2.60 mmol, 47%) of $(C_5H_5)Mo(CO)_3Cl$ (2056 (s), 1986 (vs), and 1962 (s) cm^{-1} in heptane), and a substantial amount of $[(C_5H_5)Mo(CO)_3]_2$ probably from the facile decomposition of $(C_5H_5)Mo(CO)_3H$.[9] A small amount of CH_3NH_2 was also collected during the initial sublimation of $(C_5H_5)Mo(CO)_3H$ and $(CH_3NH)_2CO$. Thus the reaction proceeds in the same manner as that of the tungsten analog.

$(C_5H_5)W(CO)_3C(O)NHCH_3$ from $(C_5H_5)W(CO)_3H$ and CH_3NCO. Onto a sample of 2.20 g (6.59 mmol) of $(C_5H_5)W(CO)_3H$ in 50 ml of THF at −196° was distilled 1.1 ml (0.831 g, 14.8 mmol) of CH_3NCO and then 0.4 ml (0.29 g, 2.87 mmol) of $(C_2H_5)_3N$. After each addition the solution was warmed to room temperature and stirred. The solution turned from pale yellow to a more intense yellow. The THF and other volatile compounds were removed at reduced pressure leaving a yellow crystalline material, whose only C–O stretching absorptions (2018 (s) and 1928 (vs) cm^{-1} in CCl_4 solvent) were those of $(C_5H_5)W(CO)_3C(O)NHCH_3$. This solid was extracted with 130 ml of warm diethyl ether. On cooling the solution to 0°, a fine yellow product formed. Further cooling to −78° gave 1.34 g of pure $(C_5H_5)W(CO)_3C(O)NHCH_3$. Although not isolated, additional product was present in the ether extract and in the residue from ether extraction. This method provides the best synthetic route to $(C_5H_5)W(CO)_3C(O)NHCH_3$.

Acknowledgment. We appreciate the support of this research by the National Science Foundation through Grant No. GP-12136.

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