Studies on Metal Carboxylates. Part X.[1] The Reactions of Group VI Hexacarbonyls with Pyridinecarboxylic Acids. Complexes of Chromium-(III), Molybdenum(III), and Tungsten-(0), -(I), and -(IV)

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The reactions of the hexacarbonyls of chromium, molybdenum, and tungsten with pyridine-2-carboxylic acid (picH) in boiling methanol afford the species $[Cr(pic)_3]$, $[Mo(pic)_3]\cdot MeOH$, and $[W(pic)_4]$. The diamagnetic tungsten(I) complex $[\{W(CO)_3(pic)\}_n]$ has also been isolated and found to be a very useful intermediate for the synthesis of a variety of tungsten carbonyl complexes of 2,2′-bipyridyl and 1,2-bis(diphenylphosphino)ethane. The reaction of $[W(CO)_6]$ with pyridine-3- and -4-carboxylic acids (nicH and isonicH, respectively) proceeds in an analogous fashion to that observed with pyridine, namely substitution without oxidation.

THE hexacarbonyls $[Mo(CO)_6]$ and $[W(CO)_6]$ react with acetic acid–acetic anhydride to afford the metal–metal bonded acetates $[Mo_2(OAc)_4]$[2] and $[\{W(OAc)_2\}_n]$.[3] The latter product has also been formulated as $[\{W_3O(OAc)_6\}_n]$.[4] For $[Mo(CO)_6]$, this reaction is of broad scope since similar products are formed with a variety of aliphatic and aromatic carboxylic acids.[2] In the case of the pyridinecarboxylic acids, for which a variety of co-ordination modes can be expected,[5] we observe quite different behaviour from that mentioned above.

The reaction of $[Cr(CO)_6]$, $[Mo(CO)_6]$, and $[W(CO)_6]$ with pyridine-2-carboxylic acid (picH) in refluxing methanol rapidly leads to the evolution of CO and H_2 and

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the formation of the highly coloured crystalline complexes $[Cr(pic)_3]$, $[Mo(pic)_3]\cdot MeOH$, and $[W(pic)_4]$, respectively. The unsolvated molybdenum(III) complex is formed when acetonitrile is used as the reaction solvent. While $[Cr(pic)_3]$ and $[W(pic)_4]$ are stable in the air once they have been isolated from the reaction mixture, $[Mo(pic)_3]$ is rapidly oxidized and was consequently handled in a nitrogen atmosphere. In the reaction between $[W(CO)_6]$ and picH, attempts were made to isolate intermediate species of the type $[W(CO)_x(pic)_y]$, but we were successful only in the case of the tungsten(I) complex $[\{W(CO)_3(pic)\}_n]$. This yellow, air-sensitive, insoluble complex was isolated when the starting materials were allowed to react in equimolar proportions. Increasing the $[W(CO)_6]$: picH proportions to 1 : 2 and 1 : 3 led only to the formation of a mixture of $[\{W(CO)_3(pic)\}_n]$ and $[W(pic)_4]$. $[\{W(CO)_3(pic)\}_n]$ is also formed upon treating $[W(pic)_4]$ with $[W(CO)_6]$ according to the following stoicheiometry:

$$[W(pic)_4] + 3[W(CO)_6] \longrightarrow 4[W(CO)_3(pic)] + 6CO$$

The paramagnetic complexes $[Cr(pic)_3]$ and $[Mo(pic)_3]$ exhibited room-temperature magnetic moments of 3.84 and 3.74 B.M., respectively, consistent with magnetically dilute t_{2g}^3 systems. Their i.r. spectra (4 000—600 cm^{-1}) are characteristic of co-ordinated pic^- with the intense $\nu(COO)_{as}$ mode located at 1 690 cm^{-1} $[Mo(pic)_3]$ and 1 675 cm^{-1} $[Cr(pic)_3]$. For the solvate $[Mo(pic)_3]\cdot MeOH$, the $\nu(COO)_{as}$ band shifts to 1 675 cm^{-1}, and sharp $\nu(OH)$ bands at 3 600 and 3 460 cm^{-1} are due to methanol. The diffuse-reflectance electronic absorption spectrum of $[Cr(pic)_3]$ exhibited its two lowest-energy ligand-field bands at 19 000 and 23 800sh cm^{-1}. These transition energies are consistent with a pseudo-octahedral chromium(III) complex and are similar to those observed with $[Cr(acac)_3]$, $[Cr(en)_3]^{3+}$, and related species.[6] For $[Mo(pic)_3]$ and its methanol solvate, the lowest energy absorption was a broad feature at *ca.* 22 000 cm^{-1}, close in energy to the lowest spin-allowed transitions in a series of 2,2′-bipyridyl complexes of molybdenum(III).[7]

The diamagnetic tungsten(IV) complex $[W(pic)_4]$ ($\chi_g = -0.25 \times 10^{-6}$ c.g.s.u. at 22 °C) has an i.r. spectrum which resembles the main features in the spectra of $[M(pic)_3]$ (M = Cr or Mo) with $\nu(COO)_{as}$ at 1 690 cm^{-1}. As with the chromium and molybdenum complexes, there was no spectral evidence for significant contamination by oxidation products containing M=O or M–OH units. The identity of this complex as an authentic derivative of tungsten(IV) was confirmed by an oxidation state titration (4.0 ± 0.1) and a study of its electronic absorption spectrum (Table 1). The latter showed a close resemblance to the solution and solid-state spectra of tetrakis-(quinolin-8-olato)tungsten(IV) (abbreviated Wq_4) and related derivatives.[8] The complex with 5-bromoquinolin-8-ol has been shown to be a dodecahedral system.[9] Intense charge-transfer bands dominate the visible region of the electronic absorption spectra of these quinolinolato-complexes and $[W(pic)_4]$, and the close similarity between the positions and intensities of these bands (Table 1) strongly suggests that $[W(pic)_4]$ also possesses a dodecahedral structure. The four major absorption bands listed in Table 1 for $[W(pic)_4]$ obeyed Beer's law over the concentration range 7.5—1.5×10^{-6}M. These spectra slowly decayed with time, and after six weeks the colour of both the methanol and aqueous solutions (*ca.* 10^{-6}M) had almost completely faded.

TABLE 1

Comparison of the electronic absorption spectra of $[W(pic)_4]$ and quinolinolato-derivatives of tungsten(IV) [a]

$[W(pic)_4]$				
N.m. [c]	MeCN [d]	MeOH [d]	$[W(q)_4]$ [b]	$[W(qBr)_4]$ [b]
16.1			14.3	14.1
			(29 000)	(33 400)
17.8	17.7	17.9	15.3	15.2
	(17 000) [e]	(16 000) [e]	(23 000)	(23 000)
~22.2sh	22.5	23.0	25.6	24.3
	(5 300)	(5 300)	(6 000)	(9 200)
~26.3sh	26.3	26.7		28.6
	(3 200)	(3 200)		(7 000)
38.5	38.1	38.1		32.3
	(21 000)	(22 000)		(6 200)

[a] Peak maxima $\times 10^{-3}$ cm^{-1}, molar extinction coefficients in parentheses. [b] Spectra recorded in benzene; see ref. 8. [c] Nujol mull. [d] Similar spectra observed in water and benzene. [e] This band is asymmetric on its low energy side.

The formulation of $[\{W(CO)_3(pic)\}_n]$ as a derivative of tungsten(I) was demonstrated by an oxidation state titration (0.95 ± 0.1), and its diamagnetism ($\chi_g = -0.18 \times 10^{-6}$ c.g.s.u.) is consistent with a metal–metal bonded structure $[W_2(CO)_6(pic)_2]$, in which the tungsten atoms conform to the EAN rule. The Nujol mull i.r. spectrum of this complex showed that bridging carbonyl groups were absent (Table 2) and that the vibrational frequencies associated with the carboxylate groups were different from those in the completely substituted complexes. The $\nu(COO)_{as}$ absorption was much sharper than in these other complexes and located at a lower frequency (1 620 cm^{-1}). Such spectral differences may be due to the presence of bridging pyridinecarboxylate groups, (I), of the type already identified in $[Cu(dipic)]\cdot 2H_2O$ (dipic = pyridine-2,6-dicarboxylato).[10]

This tungsten(I) complex was found to be very reactive towards a variety of donor molecules and its reactions with 1,2-bis(diphenylphosphino)ethane (dppe) and 2,2′-bipyridyl were explored in some detail. In the reaction with dppe, the product was either *cis*-$[W(CO)_2(dppe)_2]$ [11]

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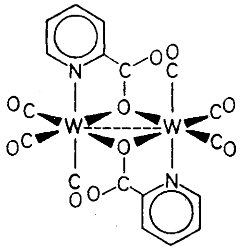
or $[W_2(CO)_6(dppe)_3]$,[12] depending upon the choice of solvent. $[W_2(CO)_6(dppe)_3]$ Has previously been isolated in only very low yield,[12] but our procedure produces it from $[W(CO)_6]$, *via* the intermediate $[\{W(CO)_3(pic)\}_n]$, in an overall yield of *ca.* 70%. In the reactions between $[\{W(CO)_3(pic)\}_n]$ and 2,2′-bipyridyl, in addition to the well known complex $[W(CO)_4(bipy)]$,[13] we also isolated the carbonyl-bridged dimer $[W_2(CO)_6(bipy)_2]$ as its methanol solvate. In a previous synthesis of this dimer by Behrens *et al.*,[14] using $[W(\eta\text{-cycloheptatriene})(CO)_3]$ as the starting material, it was found necessary to use a non-polar reaction solvent since use of a polar solvent apparently resulted in the formation of monomeric species of the type $[W(CO)_3(bipy)(solvent)]$.



(I)

TABLE 2

Infrared active ν(C-O) modes of new tungsten carbonyl complexes

Complex	Medium	Frequencies[a]
$[\{W(CO)_3(pic)\}_n]$	n.m.[b]	2 010m—s, 1 910s, 1890w, 1 880m, 1 850sh
$[W(CO)_5(nicH)]$	n.m.	2 070w, 1 970m, 1 940m—s, 1 910s, 1 890s
	MeOH	2 055m, br, 1 980w, 1 934s, 1 908m
$[W(CO)_5(isonicH)]$	n.m.	2 080w, 1 960s, 1 915vs, 1 890vs
	MeOH	2 045m, br, 1 976w, 1 934s, 1 901m
$[W(CO)_4(isonicH)_2]$	n.m.	2 080vw,[c] 2 005m—w, *ca.* 1 950w,[c] 1 865vs,[d] 1 830s
	MeOH	2 045w,[c] 2 012m, 1 935m,[c] 1 883s, 1 855m—s, *ca.* 1 830sh
$[W_2(CO)_6(bipy)_2]\cdot MeOH$	n.m.	2 010vw, 1 892vs, 1 796vs, 1 713vs[e]
$[W(CO)_3(bipy)(MeCN)]\cdot 1/2MeCN$	n.m.	1 888s, *ca.* 1 765vs, br
$[W(CO)_3(bipy)(MeCN)]\cdot 1/2Et_2O$	n.m.	1 886s, 1 770vs

[a] Band frequencies quoted to ±5 cm^{-1}. [b] n.m. = Nujol mull. [c] Due to small amount of $[W(CO)_5(isonicH)]$ contaminant. [d] Asymmetric on its high-energy side. [e] Assigned to bridging carbonyl group.

Reactions of $[W(CO)_6]$ with pyridine-3- and -4-carboxylic acid proceed in a different fashion to the related reactions with pyridine-2-carboxylic acid. Substitution without oxidation occurs to give yellow crystalline $[W(CO)_5(isonicH)]$ and $[W(CO)_5(nicH)]$, and red $[W(CO)_4(isonicH)_2]$. All three complexes possess i.r.-active ν(CO) patterns (Table 2) similar to those reported for the analogous pyridine complexes $[W(CO)_5(py)]$ and *cis*-$[W(CO)_4(py)_2]$ [15] and spectral features characteristic of hydrogen-bonded $-CO_2H$ groups,[16] namely an intense $\nu(COO)_{as}$ band between 1 710 and 1 700 cm^{-1} and sharp weak ν(O–H) absorptions in the region (2 750—2 550 cm^{-1}).

EXPERIMENTAL

All reactions were carried out under an atmosphere of nitrogen and all solvents were thoroughly dried and deoxygenated prior to use.

(a) *Preparation of Pyridinecarboxylate Complexes of Chromium, Molybdenum, and Tungsten.*—(i) $[Cr(pic)_3]$. A mixture of $[Cr(CO)_6]$ (1.10 g, 5 mmol) and pyridine-2-carboxylic acid (2.46 g, 20 mmol) in methanol (50 ml) was refluxed until $[Cr(CO)_6]$ ceased to sublime into the reflux condenser (*ca.* 6 days), from whence it was periodically returned to the reaction vessel. Red crystals of $[Cr(pic)_3]$ were filtered off, washed with methanol and ether, and dried *in vacuo* (Found: C, 51.9; H, 3.0; N, 10.3. Calc. for $C_{18}H_{12}CrN_3O_6$: C, 51.7; H, 2.9; N, 10.05%), yield 1.90 g (91%).

This product was obtained in similar yields when ethanol or acetonitrile were used as reaction solvents. However, in the latter solvent a much shorter reaction time was necessary (*ca.* 2 days).

(ii) $[Mo(pic)_3]\cdot MeOH$. This complex was prepared as yellow–orange needles in 38% yield by a procedure similar to that described in (i), with a reaction time of 1.5 days (Found: C, 46.2; H, 2.5; Mo, 19.2; N, 8.65. Calc. for $C_{19}H_{16}MoN_3O_7$: C, 46.2; H, 3.3; Mo, 19.4; N, 8.5%).

The unsolvated complex was prepared when acetonitrile was used as solvent. A reaction time of 1 day gave this product in 66% yield (Found: C, 46.5; H, 2.7; N, 9.3. Calc. for $C_{18}H_{12}MoN_3O_6$: C, 46.8; H, 2.6; N, 9.1%).

(iii) $[W(pic)_4]$. This complex was prepared as amber crystals using procedure (i), with a reaction time of 1—4 days and methanol, ethanol, or acetonitrile as the reaction solvent (Found: C, 42.1; H, 2.4; N, 8.0; W, 27.4. Calc. for $C_{24}H_{16}N_4O_8W$: C, 42.9; H, 2.4; N, 8.3; W, 27.35%), yield 60—70%.

(iv) $[\{W(CO)_3(pic)\}_n]$. A mixture of $[W(CO)_6]$ (4.23 g, 12 mmol) and picH (1.48 g, 12 mmol) in ethanol (60 ml) was refluxed for 3 days. The insoluble yellow reaction product was filtered off, washed with ethanol (6 × 5 ml), and dried *in vacuo* (Found: C, 27.6; H, 1.2; N, 3.8; W, 47.1. Calc. for $C_9H_4NO_5W$: C, 27.7; H, 1.0; N, 3.6; W, 46.8%), yield 3.59 g (77%). This complex is air-sensitive and darkens upon exposure to the atmosphere. It is virtually insoluble in water and most common organic solvents except dimethylformamide in which it dissolves to form a very dark green solution.

(v) $[W(CO)_5(nicH)]$. By a procedure similar to that described in (i), $[W(CO)_6]$ (1.76 g, 5 mmol) was treated with pyridine-3-carboxylic acid (0.615 g, 5 mmol) in methanol (50 ml) for 3 days. The red-orange reaction solution was filtered to remove a small amount of unidentified pyrophoric

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brown solid. Deoxygenated water (200 ml) was added to the filtrate to precipitate yellow crystals of the complex. These were recrystallized twice from aqueous methanol (Found: C, 29.7; H, 1.2; N, 3.3; W, 40.6. Calc. for $C_{11}H_5NO_7W$: C, 29.6; H, 1.1; N, 3.1; W, 41.1%), yield 0.67g (30%).

This same product was isolated when the $[W(CO)_6]$: nicH mole proportions were increased to 1 : 4.

(vi) $[W(CO)_5(isonicH)]$ and $[W(CO)_4(isonicH)_2]$. The reaction of $[W(CO)_6]$ (3.52 g, 10 mmol) with pyridine-4-carboxylic acid (3.69 g, 30 mmol) in methanol afforded a deep red solution. The reaction was stopped after 5 days, the solution filtered to remove any unchanged starting materials, and deoxygenated water (400 ml) was added to the filtrate. A Soxhlet extraction of the insoluble product with dichloromethane for 5 days under nitrogen left insoluble dark red $[W(CO)_4(isonicH)_2]$ in the thimble. The yellow dichloromethane extract was evaporated to dryness to afford bright yellow $[W(CO)_5(isonicH)]$. Both complexes were recrystallized from aqueous methanol (Found: C, 30.1; H, 1.5; N, 3.35; W, 40.2 Calc. for $C_{11}H_5NO_7W$: C, 29.6; H, 1.1; N, 3.1; W, 41.1%. Found: C, 34.9; H, 1.8; N, 4.9; W, 34.2. Calc. for $C_{16}H_{10}N_2O_8W$: C, 35.45; H, 1.9; N, 5.2; W, 33.9%). Yield, $[W(CO)_4(isonicH)_2]$, 1.59 g (29%); $[W(CO)_5(isonicH)]$, 1.71 g (38%).

(b) *Reactions of* $[\{W(CO)_3(pic)\}_n]$ *with* 2,2′-*Bipyridyl and* 1,2-*Bis(diphenylphosphino)ethane*.—(i) $[W(CO)_4(bipy)]$. When a mixture of $[\{W(CO)_3(pic)\}_n]$ and 2,2′-bipyridyl (1 : 1, 1 : 2, or 1 : 3 mole proportions) was stirred in methanol for 70 h, the complex $[W(CO)_4(bipy)]$ was isolated in 70% yield. Its i.r. spectrum was identical with that of an authentic sample of this complex.[13]

(ii) $[W_2(CO)_6(bipy)_2]$. The reaction between $[\{W(CO)_3(pic)\}_n]$ (0.39 g, 1 mmol) and 2,2′-bipyridyl (0.156 g, 1 mmol) in methanol (20 ml) at room temperature for between 17 and 26 h produced a precipitate of black $[W_2(CO)_6(bipy)_2]\cdot MeOH$ (Found: C, 35.85; H, 2.8; N, 6.4; W, 43.0. Calc. for $C_{26}H_{16}N_4O_6W_2$: C, 36.8; H, 2.3; N, 6.4; W, 41.8%), yield 0.263 g (60%); ν(O-H) of 'lattice' methanol was located at 3 310 cm^{-1} in the i.r. spectrum of this complex.

(iii) $[W(CO)_3(bipy)(MeCN)]\cdot 1/2$ solvent. When acetonitrile was used as the reaction solvent, any of the reaction conditions described in (b) (i) and (ii) afforded an insoluble brown powder which was filtered off and thoroughly washed with acetonitrile. The reaction filtrate and acetonitrile washings were combined and then divided into equal volumes [portions (a) and (b)]. Portion (a) was reduced to low volume to produce crystals of $[W(CO)_3(bipy)(MeCN)]\cdot 1/2MeCN$ (Found: C, 39.8; H, 2.7; N, 10.0. Calc. for $C_{16}H_{12.5}N_{3.5}O_3W$: C, 39.6; H, 2.6; N, 9.9%). This product exhibited a weak broad $\nu(C\equiv N)$ band at *ca.* 2 260 cm^{-1} in its i.r. spectrum.

Portion (b) was treated with an excess of diethyl ether to cause the formation of black needles of $[W(CO)_3(bipy)(MeCN)]\cdot 1/2Et_2O$ (Found: C, 41.0; H, 3.1; N, 8.5. Calc. for $C_{17}H_{16}N_3O_{3.5}W$: C, 40.7; H, 3.2; N, 8.4%). In addition to a weak $\nu(C\equiv N)$ band at *ca.* 2 260 cm^{-1}, the i.r. spectrum of this product showed a moderately intense $\nu(C\text{–}O\text{–}C)_{as}$ absorption at 1 113 cm^{-1} due to the 'lattice' diethyl ether.

(iv) $[W_2(CO)_6(dppe)_3]$. $[\{W(CO)_3(pic\}_n]$ (0.390 g, 1 mmol) and dppe (0.796 g, 2 mmol) were added to refluxing methanol (20 ml) and the reaction mixture was stirred for 90 h. The insoluble tan product was filtered off and recrystallized from dichloromethane–hexane (Found: C, 58.5; H, 4.4; P, 10.5. Calc. for $C_{84}H_{72}O_6P_6W_2$: C, 58.3; H, 4.2; P, 10.7%), yield 0.83 g (96%). The i.r. spectrum of this complex was identical to that reported previously.[12]

(v) cis-$[W(CO)_2(dppe)_2]$. The reaction between $[\{W(CO)_3(pic)\}_n]$ (0.390 g, 1 mmol) and dppe (0.796 g, 2 mmol) for 21 h in refluxing benzene (15 ml) afforded a dark brown solution which was allowed to cool to room temperature and then filtered. The filtrate was evaporated to very low volume, treated with dichloromethane (50 ml), refiltered, and finally mixed with an excess of diethyl ether. This afforded bright yellow *cis*-$[W(CO)_2(dppe)_2]$ which was filtered off and dried *in vacuo* (Found: C, 61.6; H, 4.8; P, 11.5. Calc. for $C_{54}H_{48}O_2P_4W$: C, 62.6; H, 4.7; P, 11.95%), yield 0.183 g (18%). The i.r. spectrum of this complex was identical to that reported in the literature.[11]

Physical Measurements.—These were carried out as described previously.[17]

This work was supported in part by the National Science Foundation and by the Camille and Henry Dreyfus Foundation.

[5/1057 *Received, 2nd June*, 1975]

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