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STUDIES ON METAL CARBOXYLATES

XI *. REACTIONS OF RHENIUM CARBONYL WITH PICOLINIC ACID AND OF THE TUNGSTEN(I) COMPLEX $[W(CO)_3(pic)]_n$ WITH MONODENTATE TERTIARY PHOSPHINES

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Summary

The reactions of the tungsten(I) complex of picolinic acid $[W(CO)_3(pic)]_n$ with certain monodentate tertiary phosphines affords a convenient route to complexes of the types $W(CO)_3(PR_3)_3$ and $HW(CO)_2(PR_3)_2(pic)$. The latter hydrido complexes of tungsten(II) have been characterized by infrared and NMR spectroscopy. The reactions of $Re_2(CO)_{10}$ with picolinic acid have also been investigated and the new series of rhenium(I) derivatives of the types $Re(CO)_3(L)(pic)$, where L = py, 4-Ph-py, PPh_3 or dppe, and $Re(CO)_2(L')_2(pic)$, where L′ = PPh_3 or 1/2dppe, have been isolated and characterized.

Introduction

We have recently shown that the Group VI hexacarbonyls react with excess pyridine-2-carboxylic acid, otherwise known as picolinic acid (abbreviated picH), under relatively mild conditions to produce the metal picolinates $Cr(pic)_3$, $Mo(pic)_3$, and $W(pic)_4$ [1]. Furthermore, in the case of tungsten we were able to isolate the partially substituted tungsten(I) carbonyl complex $[W(CO)_3(pic)]_n$ and found it to be an excellent intermediate for the high yield synthesis of a variety of tungsten carbonyl complexes of bidentate nitrogen and phosphorus ligands [1]. We now report on reactions of $[W(CO)_3(pic)]_n$ with several monodentate phosphorus and nitrogen donors, and on reactions of picolinic acid with rhenium carbonyl.

Results and discussion

The reactions of $[W(CO)_3(pic)]_n$ with monodentate ligands parallel for the most part its reactions with the analogous bidentate ligands, namely loss of the

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* For part X see ref. 1.

picolinate ligand and reduction of tungsten to tungsten(0). Thus, $[W(CO)_3(pic)]_n$ rapidly reacts with pyridine and several monodentate tertiary phosphines to produce neutral tungsten(0) complexes of the type *fac*-$W(CO)_3L_3$ (Table 1). Since these derivatives, together with the complexes *cis*-$W(CO)_2(dppe)_2$, $W_2(CO)_6(dppe)_3$, $W_2(CO)_6(bipy)_2$ and $W(CO)_3(bipy)(MeCN)$, where dppe = 1,2-bis(diphenylphosphino)ethane and bipy = 2,2'-bipyridyl [1], can all be easily prepared from $[W(CO)_3(pic)]_n$, this reagent offers considerable advantages over the variety of preparative procedures which have previously been used to prepare these [2—8] and related tungsten(0) carbonyl complexes. Most of the previous syntheses have involved the use of $[W(\eta\text{-cycloheptatriene})(CO)_3]$ as the starting material. In view of the low yield with which this latter complex is prepared from $W(CO)_6$ [9], $[W(CO)_3(pic)]_n$ would seem to be a much more desirable starting material for the synthesis of these and related complexes.

In the case of the reactions of $[W(CO)_3(pic)]_n$ with triphenylphosphine and dimethylphenylphosphine in refluxing methanol, the tungsten(II) hydrido complexes $HW(CO)_2(PPh_3)_2(pic)$ and $HW(CO)_2[P(CH_3)_2Ph]_2(pic)$ were isolated. We first thought that these products were the tungsten(I) derivatives $W(CO)_2(PR_3)_2(pic)$. However, magnetic susceptibility measurements showed them to be diamagnetic, a property which is inconsistent with their formulation as monomeric d^5 tungsten(I) species. When molecular weight determinations in chloroform and benzene showed the triphenylphosphine complex to be monomeric, we suspected that they were in reality diamagnetic hydride derivatives of tungsten(II). The measurement of their NMR spectra in the region τ 10—25 ppm confirmed this suspicion (see Table 1 and Fig. 1). The ^1H NMR spectra of these complexes in

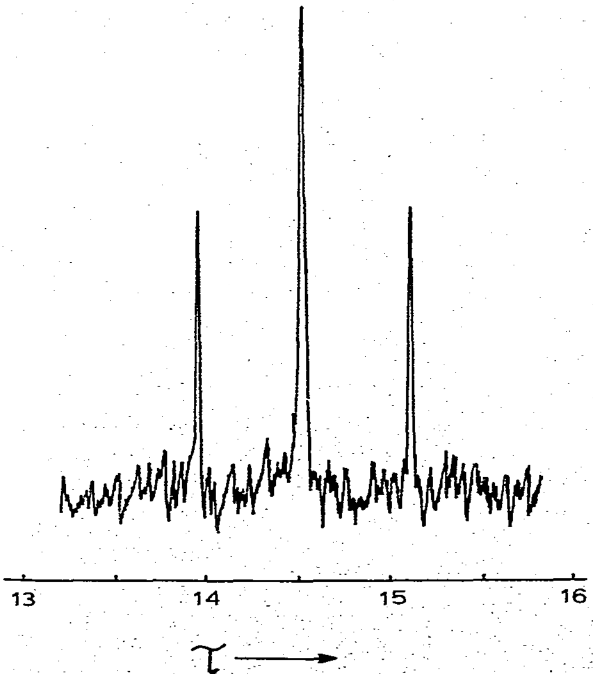


Fig. 1. NMR spectrum of the hydride moiety for a $CDCl_3$ solution of $HW(CO)_2[P(CH_3)_2Ph]_2(pic)$. The triplet is centered at τ 14.53 ppm with $J(^{31}P—^1H)$ 35 Hz.

TABLE 1

INFRARED SPECTRA AND HYDRIDE NMR CHEMICAL SHIFTS OF TUNGSTEN CARBONYL COMPLEXES PREPARED FROM $[W(CO)_3(pic)]_n$

Complex	Medium	IR (cm^{-1})			NMR [c] Hydride chemical shifts (τ, ppm)
		$\nu(CO)$	$\nu_{as}(COO^-)$	$\nu_s(COO^-)$	
$W(CO)_3(py)_3$	*a*	1885s 1733vs(br)	—	—	—
$W(CO)_3[P(CH_3)_2Ph]_3$	*a*	1910s 1815vs(br) 1780m(sh)	—	—	—
$W(CO)_3[P(CH_3)Ph_2]_3$	*a*	1925s 1830vs 1805s	—	—	—
$W(CO)_3(PPh_3)_3$	*a*	1925s 1890w 1830vs	—	—	—
$HW(CO)_2[P(CH_3)_2Ph]_2(pic)$	*a*	1898s 1865w [d] 1800vs	1665m—s	1325m—w	14.53[$J(^{31}P—^1H)$ 35 Hz]
	b	1900vs 1805s			
$HW(CO)_2(PPh_3)_2(pic)$	*a*	1900s 1870w [d] 1810vs	1670m—s	1320m—w	13.48[$J(^{31}P—^1H)$ 34 Hz]
	b	1895vs ~1860vw [d] 1815s			

[a] Measured as nujol mull. [b] Measured in CH_2Cl_2. [c] Measured in $CDCl_3$. [d] Assigned to $\nu(W—H)$; see ref. 15.

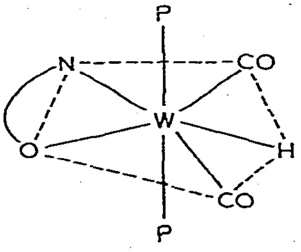
TABLE 2

INFRARED SPECTRA AND ^1H NMR CHEMICAL SHIFTS OF RHENIUM CARBONYL COMPLEXES OF PICOLINIC ACID

Complex	IR [a] (cm^{-1})			NMR [b] Phenyl chemical shifts (τ, ppm)
	$\nu(CO)$	$\nu_{as}(COO^-)$	$\nu_s(COO^-)$	
$Re(CO)_3(py)(pic)$	2022s 1913vs 1890vs	1659m—s	1341m	—
$Re(CO)_3(4\text{-}Ph\text{-}py)(pic)$	2020s 1900vs 1875vs	1665m—s	1332m	2.47
$Re(CO)_3(PPh_3)(pic)$	2022s 1930s 1910s	1670m—s	1332m	2.65 [c] 2.73 [c]
$Re(CO)_3(dppe)(pic)$	2020s 1940s 1900s	1666sh 1635m	1340m—s	2.57 ~2.87
$Re(CO)_2(PPh_3)_2(pic) \cdot H_2O$	1922s 1855s	1659m—s 1645(sh)	1345w 1330w	2.72
$Re(CO)_2(dppe)(pic)$	1920s 1840s	1660m—s 1645(sh)	1340w	2.63

[a] Measured as nujol mulls. [b] Measured in $CDCl_3$. [c] These resonances are very sharp and narrow.

$CDCl_3$ showed a triplet centered between about τ 13.5 and 14.5 ppm with $J(^{31}P-^{1}H)$ 34—35 Hz. These observations contrast with those for the related seven-coordinate hydrides *trans*-$[HM(CO)_2(dpm)_2]^+$, where M = Cr, Mo or W and dpm = bis(diphenylphosphino)methane [10], in which a triplet of triplets associated with the hydride was observed. This latter result implies that the hydride is coupled to two inequivalent pairs of phosphorus atoms. On the other hand, in the case of $HW(CO)_2(PR_3)_2$(pic), the pattern is characteristic of that expected for coupling to two equivalent phosphorus atoms. Provided this molecule is not fluxional in nature, thereby leading to an equivalence of the phosphorus atoms, this observation is consistent with a pentagonal bipyramidal geometry, such as that depicted in structure I, rather than the capped octahedral or trigonal prismatic stereochemistries which are usually favored by seven-coordinate molybdenum(II) and tungsten(II) carbonyl complexes [11—13]. Since we are currently pursuing an investigation of the detailed stereochemistry of these complexes by means of a single crystal X-ray structure analysis of $HW(CO)_2[P(CH_3)_2Ph]_2$(pic), more detailed discussions are deferred until a later date.



(I)

In the generation of the hydride complexes, the solvent may be the source of hydrogen. However, since $HW(CO)_2(PPh_3)_2$(pic) can be prepared using either methanol or benzene as the solvent, an alternative mechanism involving hydrogen abstraction from the phosphine ligand is also a possibility.

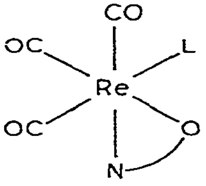
The results of our investigations of the Group VI metal picolinates, and the reactions of $[W(CO)_3(pic)]_n$ to produce both tungsten (0) complexes and the tungsten(II) hydrides, prompted us to extend our studies of the reactions of picolinic acid to other metal carbonyls. Accordingly, we have examined the reactions of picolinic acid with rhenium carbonyl as a possible route to low oxidation state rhenium complexes.

When rhenium carbonyl was reacted with picolinic acid under conditions similar to those used to prepare the Group VI picolinates, virtually no reaction was observed even when the reflux time was extended to one week. However, when a mixture of the solid reactants was melted, the air-stable crystalline complex $Re(CO)_3$(py)(pic), quickly formed. In this reaction, pyridine is generated by the thermal decarboxylation of picolinic acid. Increased yields of this complex were achieved by the addition of pyridine at the start of the reaction. Alternatively, the related 4-phenylpyridine complex $Re(CO)_3$(4-Ph-py)(pic) can be made in almost quantitative yield by addition of this much less volatile substituted pyridine.

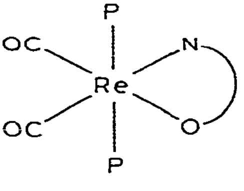
When either of these products is mixed with the phosphorus donors triphenylphosphine or bis(diphenylphosphino)ethane in refluxing methanol, the pyridine is replaced to form $Re(CO)_3(PPh_3)$(pic) or $Re(CO)_3$(dppe)(pic), respectively. In the latter complex, dppe is bound in a monodentate fashion. In the case of triphenylphosphine, a short reaction time (ca. 2 h) is critical in order to avoid significant contamination by $Re(CO)_2(PPh_3)_2(pic)$. With dppe, contamination was not a problem, even when the reaction time was extended to 48 h. However, under the more rigorous conditions of a melt reaction at 200°C, further replacement of CO by both ligands is observed, producing the bright yellow complexes $Re(CO)_2(PPh_3)_2(pic)$ and $Re(CO)_2(dppe)(pic)$, respectively.

Molecular weight determinations indicate that the rhenium complexes are monomeric, and their diamagnetism confirms that they are authentic rhenium(I) derivatives. Due to the low symmetry of these complexes, infrared spectroscopy (Table 2) will not easily distinguish between the possible configurations. However, *trans*-effect arguments would support a structure in which the greatest possible number of carbonyl groups are mutually *cis*. Thus the most likely configuration of $Re(CO)_3(L)(pic)$ complexes is *facial* (structure II), where L = py, 4-Ph-py, PPh_3 or monodentate dppe. The ^1H NMR spectrum of $Re(CO)_3(dppe)(pic)$ is consistent with the monodentate nature of dppe. Multiplet resonances associated with the phenyl groups are observed at τ 2.57 ppm, due to the coordinated end of the ligand, and at τ 2.87 ppm, due to the uncoordinated end. These chemical shifts can be compared with those for bidentate dppe in $Re(CO)_2(dppe)(pic)$ (one multiplet phenyl resonance at τ 2.63 ppm) and free dppe (one multiplet resonance at τ 2.73 ppm).

Since phosphines generally have much greater *trans* labilizing effects than nitrogen or oxygen donors, the most likely configuration for $Re(CO)_2(PPh_3)_2(pic)$ is that shown in structure III. Crystallographic studies have shown that this is the preferred configuration in other dicarbonyl species of this type [14].



(II)



(III)

Of the three possible structures for monomeric $Re(CO)_2(dppe)(pic)$, those with a *cis*-arrangement of carbonyl groups are favored by the infrared spectral data (Table 2).

Experimental

All reactions were carried out under a nitrogen atmosphere and all solvents were thoroughly dried and deoxygenated prior to use. The complex $[W(CO)_3(pic)]_n$ was prepared as described previously [1] and $Re_2(CO)_{10}$ was obtained from Strem Chemicals Inc.

A. Reactions of $[W(CO)_3(pic)]_n$ with pyridine and monodentate tertiary phosphines

(i) $W(CO)_3(py)_3$. $[W(CO)_3(pic)]_n$ (0.78 g, 2.0 mmol) and pyridine (5 ml) were

stirred at room temperature for 10 min. The resulting dark red microcrystalline precipitate was filtered off, washed with pyridine (5 × 3 ml) and ether (5 × 5 ml) and then dried in vacuo for 48 h. Yield, 0.831 g (76%). Found: C, 43.05; H, 3.24; N, 8.29. $C_{18}H_{15}N_3O_3W$ calcd.: C, 42.80; H, 2.99; N, 8.32%.

(ii) $W(CO)_3(PPh_3)_3$. A methanol slurry of $[W(CO)_3(pic)]_n$ (0.390 g, 1.0 mmol) and triphenylphosphine (1.05 g, 4.0 mmol) was stirred at 25°C for 2 days. The resulting precipitate was thoroughly washed with methanol (5 × 5 ml), benzene (5 × 5 ml), and petroleum ether (3 × 5 ml) to give 0.545 g (52%) of an air-stable yellow-tan powder. This complex was identified by a comparison of its infrared spectrum with that described in the literature for a sample of this complex prepared by a different procedure [6].

A quantity of the tungsten(II) hydrido complex $HW(CO)_2(PPh_3)_2(pic)$ (see *A(iii)*) was isolated from the above benzene washings by the addition of an excess of petroleum ether. Yield, 0.16 g (18%).

(iii) $HW(CO)_2(PPh_3)_2(pic)$. A mixture of $[W(CO)_3(pic)]_n$ (1.17 g, 3.0 mmol) and triphenylphosphine (1.57 g, 6.0 mmol) in 20 ml methanol was refluxed for 24 h. The reaction mixture was filtered to obtain 2.42 g (91%) of orange crystals which were washed with methanol (5 × 10 ml) and ether (2 × 10 ml). Found: C, 59.38; H, 3.98; N, 1.60; P, 6.94; mol. wt. in benzene, 935; mol. wt. in chloroform, 849. $C_{44}H_{35}NO_4P_2W$ calcd.: C, 59.54; H, 3.97; N, 1.58; P, 6.98%; mol. wt., 888.

This complex was also prepared in high yield with refluxing benzene as the reaction solvent and using 1 : 4 mole proportions of reactants. The product was precipitated from solution by the addition of petroleum ether. In the solid state this complex darkens slowly on exposure to air (1—3 days). However, its solutions in chloroform, dichloromethane and benzene are much more sensitive and decomposition is apparent within 1—2 min.

(iv) $W(CO)_3[P(CH_3)_2Ph]_3$. A mixture of $[W(CO)_3(pic)]_n$ (0.78 g, 2.0 mmol) and dimethylphenylphosphine (1.0 ml, >8 mmole) in 15 ml methanol was refluxed for 12 h. Filtration and repeated washing of the insoluble product with methanol (4 × 5 ml), followed by evacuation left 0.67 g (49%) of pale yellow needles. Found: C, 47.40; H, 4.91; P, 13.34. $C_{27}H_{33}P_3O_3W$ calcd.: C, 47.53; H, 4.87; P, 13.62%.

(v) $HW(CO)_2[P(CH_3)_2Ph]_2(pic)$. The filtrate and wash solutions of reaction *A(iv)* were added to 100 ml of water, causing precipitation of 0.28 g (22%) of deep orange crystals. After 2 h these were collected by filtration, thoroughly washed with water (10 × 5 ml), and dried in vacuo for 24 h. Found: C, 44.77; H, 4.53; N, 2.31; P, 9.89. $C_{24}H_{27}NO_4P_2W$ calcd.: C, 45.09; H, 4.26; N, 2.19; P, 9.69%.

(vi) $W(CO)_3[P(CH_3)Ph_2]_3$. This complex was prepared in 47% yield by a procedure similar to that used in *A(iv)*.

B. Reactions of $Re_2(CO)_{10}$ *with picolinic acid*

(i) $Re(CO)_3(py)(pic)$. (a) A mixture of $Re_2(CO)_{10}$ (0.98 g, 1.5 mmol) and picolinic acid (0.80 g, 6.5 mmol) was heated in a test tube for 30 min at 170—190°C. The resulting brown melt was allowed to cool, then recrystallized twice from CH_2Cl_2/petroleum ether to produce a pale yellow microcrystalline powder (0.32 g, 23% yield). Found: C, 35.70, 35.48; H, 2.03, 1.86; N, 5.80, 5.44;

mol. wt. in chloroform, 483. $C_{14}H_9N_2O_5Re$ calcd.: C, 35.67; H, 1.92; N, 5.94%; mol. wt., 471. (b) When the above reaction was carried out in the presence of excess pyridine, the product was formed in higher yield (39%). It was purified by dissolving the reaction mixture in CH_2Cl_2 and extracting this 3 times with water, in order to remove excess pyridine and picolinic acid. The desired product was precipitated as fine yellow needles by the addition of petroleum ether to the CH_2Cl_2 solution.

(ii) Re(CO)₃(4-Ph-py)(pic). A mixture of $Re_2(CO)_{10}$ (0.98 g, 1.5 mmol), picolinic acid (0.80 g, 6.5 mmol) and 4-phenylpyridine (1.00 g, 6.4 mmol) was heated in a test tube for 1 h at 170—190°C. The resulting red melt was treated in a manner similar to *B*(*i*)(b) to produce 1.49 g (90% yield) of pale yellow needles. Found: C, 43.47; H, 2.74; N, 5.18. $C_{20}H_{13}N_2O_5Re$ calcd.: C, 43.71; H, 2.75; N, 5.10%.

(iii) Re(CO)₃(PPh₃)(pic). A mixture of $Re(CO)_3$(4-Ph-py)(pic) (0.31 g, 0.56 mmol) and triphenylphosphine (1.3 g, 5 mmol) was refluxed in methanol (50 ml) for 2 h. The solvent was then removed by evaporation, and the solid was thoroughly washed with ether (8 X 10 ml). The yield of very pale yellow powder was 0.319 g (87%). A $CHCl_3$ solution was purified by chromatography on Al_2O_3 prior to microanalysis. Found: C, 49.25; H, 3.16; N, 2.12; P, 4.99. $C_{27}H_{19}NO_5PRe$ calcd.: C, 49.54; H, 2.93; N, 2.14; P, 4.73%. A reaction time of 14 h produced significant contamination by $Re(CO)_2(PPh_3)_2$(pic).

This product can also be prepared from $Re(CO)_3$(py)(pic) in similar yields to those obtained using the related 4-phenylpyridine complex as the starting material.

(iv) Re(CO)₂(PPh₃)₂(pic) · H₂O. A mixture of $Re(CO)_3$(py)(pic) (0.235 g, 0.50 mmol) and triphenylphosphine (0.42 g, 1.5 mmol) was heated in a test tube at 190—200°C for 30 min. The resulting melt was then treated in a manner similar to *B(i)*(b), producing 0.368 g (67% yield) of bright yellow powder. This was dried in vacuo for 24 h prior to microanalysis. Found: C, 58.18; H, 4.00; N, 1.62; P, 7.00; mol. wt. in $CHCl_3$, 881. $C_{44}H_{36}NO_5P_2Re$ calcd.: C, 58.27; H, 4.00; N, 1.54; P, 6.83%; mol. wt., 907. The infrared spectrum showed a weak absorption at 3440 cm^{-1} due to "lattice" H_2O.

This complex was also prepared by reacting $Re_2(CO)_{10}$, picolinic acid, and excess triphenylphosphine directly at 190—200°C for 1 h, followed by a work-up procedure similar to that described above.

(v) Re(CO)₃(dppe)(pic). $Re(CO)_3$(4-Ph-py)(pic) (0.55 g, 1 mmol) and dppe (0.80 g, 2 mmol) were treated in refluxing methanol for 2 days. After filtration to remove unreacted dppe, the solution was evaporated to dryness. The crude product was then dissolved in 10 ml of CH_2Cl_2 and precipitated with 100 ml of petroleum ether to give 0.557 g (70% yield) of pale yellow powder, which was further purified by chromatography ($CHCl_3/Al_2O_3$) prior to microanalysis. Found: C, 52.74; H, 3.72; N, 2.05; P, 7.74; mol. wt. in chloroform, 805. $C_{35}H_{28}NO_5P_2Re$ calcd.: C, 53.16; H, 3.57; N, 1.77; P, 7.83%; mol. wt., 791.

(vi) Re(CO)₂(dppe)(pic) · ½ CHCl₃. This complex was prepared as a bright yellow powder in 76% yield by a procedure similar to that described in *B(iv)*, starting with $Re(CO)_3$(4-Ph-py)(pic) and excess dppe. The complex was further purified by chromatography ($CHCl_3/Al_2O_3$) prior to microanalysis. Found: C, 50.27; H, 3.70; N, 1.65; P, 7.80. $C_{34.5}H_{28.5}Cl_{1.5}NO_4P_2Re$ calcd.: C, 50.38; H, 3.49; N, 1.70;

P, 7.53%. The infrared spectrum showed absorptions at 1215w and 760m cm^{-1} due to "lattice" $CHCl_3$.

The unsolvated complex $Re(CO)_2(dppe)(pic)$ could be obtained by crystallization from chloroform/petroleum ether. Found: C, 53.60; H, 3.90; N, 1.82; P, 8.00. $C_{34}H_{28}NO_4P_2Re$ calcd.: C, 53.54; H, 3.70; N, 1.84; P, 8.12%. The infrared spectrum of this complex showed no evidence for chloroform, but is otherwise identical to that of the solvated complex.

Physical Measurements.

Infrared spectra were recorded on Beckman Acculab-6 and IR-12 spectrophotometers and NMR spectra on Varian A-60A and Perkin—Elmer R-32 (90 MHz) spectrometers.

Microanalyses and molecular weight determinations were performed by Dr. C.S. Yeh of the Microanalytical Laboratory, Purdue University.

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