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Preliminary communication

NITRATO(TRIPHENYLPHOSPHINE) COMPLEXES OF THE PLATINUM METALS; DETECTION OF TRIPHENYLPHOSPHINE OXIDE LIGANDS

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Summary

Reactions of some platinum group metal triphenylphosphine complexes with nitric acid afford nitrato(triphenylphosphine) derivatives in good yield; the complex "$Rh(NO_3)(NO)_2(OPPh_3)_2$" is positively identified as $[Rh(NO_3)_2(NO)(PPh_3)_2]$.

As part of our work on labile oxygen donor ligands in platinum metal chemistry, we have prepared a series of new nitrato derivatives (see Table 1) by the reaction of suitable triphenylphosphine complexes with nitric acid. The products $[Ru(NO_3)_2(CO)_2(PPh_3)_2]$, $[Rh(NO_3)_2(NO)(PPh_3)_2]$ $[Ir(NO_3)_2(NO)(PPh_3)_2]$ and $[Pt(NO_3)_2(PPh_3)_2]$ are obtained by treating the complexes $[Ru(CO)_3(PPh_3)_2]$, $[Rh(NO)(PPh_3)_3]$, $[Ir(NO)(CO)(PPh_3)_2]$ and $[Pt(PPh_3)_4]$, respectively, with dilute aqueous nitric acid in methanol under reflux. The action of neat concentrated nitric acid on $[RuH_2(CO)(PPh_3)_3]$ and $[OsH_2(CO)(PPh_3)_3]$ affords the complexes $[Ru(NO_3)_2(CO)(PPh_3)_2]$ and $[Os(NO_3)_2(CO)(PPh_3)_2]$, whereas in cold benzene concentrated nitric acid reacts with the complexes $[RhH(CO)(PPh_3)_3]$ and $[IrH(CO)(PPh_3)_3]$ to yield intractable products tentatively formulated as $[Rh(NO_3)_3(PPh_3)_2]$ and $[Ir(NO_3)_3(PPh_3)_2]$.

The ruthenium and osmium dinitrates $[M(NO_3)_2(CO)(PPh_3)_2]$ react with carbon monoxide in boiling ethanol to form the dicarbonyls $[M(NO_3)_2(CO)_2(PPh_3)_2]$, and undergo facile alcoholysis followed by β-elimination to yield new hydrido species $[MH(NO_3)(CO)(PPh_3)_2]$. The latter reaction provides the basis for a catalytic alcohol dehydrogenation process analogous to, but less efficient than, that observed for the corresponding perfluorocarboxylates $[M(OCOCF_3)_2(CO)(PPh_3)_2]$ [1]. The osmium species $[OsH(NO_3)(CO)(PPh_3)_2]$ reacts with carbon monoxide to form $[OsH(NO_3)(CO)_2(PPh_3)_2]$, however, the analogous ruthenium complex affords a mixture of products even on mild carbonylation. The products

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TABLE 1

FORMULAE, COLOUR AND SPECTRAL DATA^a OF THE NITRATO DERIVATIVES OBTAINED

Product	Colour	NMR spectra		Infrared spectra ν(cm^{-1})	
		τ(MH) (ppm)	J(PH) (Hz)	ν(MH)	ν(CO)/(NO)
$Ru(NO_3)_2(CO)(PPh_3)_2$	yellow				1986s
$RuH(NO_3)(CO)(PPh_3)_2$	white	26.41(t)	19.3	2098w	1928s
$Ru(NO_3)_2(CO)_2(PPh_3)_2$	white				2012s 2068s
$Os(NO_3)_2(CO)(PPh_3)_2$	yellow				1970s
$OsH(NO_3)(CO)(PPh_3)_2$	white	29.82(t)	16.7	2200w	1920s
$Os(NO_3)_2(CO)_2(PPh_3)_2$	white				1985s 2059s
$OsH(NO_3)(CO)_2(PPh_3)_2$	white	12.53(t)	20.0	1938s	1983s 2054s
$Rh(NO_3)_2(NO)(PPh_3)_2$	green				1640s(br)
$Rh(NO_3)_3(PPh_3)_2$	yellow				
$Ir(NO_3)_2(NO)(PPh_3)_2$	pale green				1580
$Ir(NO_3)_3(PPh_3)_2$	pale yellow				

^{a}Infrared spectra obtained using nujol mulls; s, strong; w, weak, (br), broad. NMR spectra taken in $CDCl_3$; t, triplet.

are air-stable crystalline solids which possess analytical and spectroscopic data consistent with the formulations given in Table 1; all show infrared bands at 1590—1495, 1285—1225, 1010—950 and 830—760 cm^{-1} attributable to coordinated nitrate.

The green rhodium complex [$Rh(NO_3)_2(NO)(PPh_3)_2$] is identical with the product obtained by previous workers [2] from the reaction of [$RhH(PPh_3)_4$] with nitric acid, and tentatively formulated by them as a phosphine oxide derivative "[$Rh(NO_3)(NO)_2(OPPh_3)_2$]" on the basis of mass spectra (high abundance Ph_3PO^+ ions, absence of PPh_3^+ ions) and infrared data [ν(P=O) 1098vs cm^{-1}]. In order to establish the structure of the rhodium nitrate complex we have compared its spectroscopic properties with those of the related perfluorocarboxylates [$Rh(OCOR_F)_2(NO)(PPh_3)_2$] [3] for which triphenylphosphine oxide formulations are excluded by analytical data. The nitrate and perfluorocarboxylato complexes have very similar ultraviolet and visible spectra and all display rhodium—phosphorus NMR couplings [^1J(RhP) ca. 117 Hz] indicative of a direct Rh—P linkage [^1J(RhP) values reported [4] for tertiary phosphine bound to rhodium(III) are generally in the range 80—130 Hz]. Furthermore, the nitrato complex reacts with hydrogen chloride to generate the known dichloride [$RhCl_2(NO)(PPh_3)_2$] in good yield. We therefore conclude that the nitrato complex is correctly formulated as [$Rh(NO_3)_2(NO)(PPh_3)_2$], and that the conclusions drawn from the mass spectra and infrared data are erroneous [2].

Although occurrence of triphenylphosphine oxide parent ions and fragmentation products in the mass spectrum is obviously consistent with the presence of triphenylphosphine oxide ligands it is open to other interpretation. Given the relatively poor coordinating power of triphenylphosphine oxide towards the platinum group metals, it seems probable that this species is either present as a trace impurity or is generated in the spectrometer by interaction of triphenylphosphine with nitrate ions or traces of oxygen. In our hands the complexes $[Rh(NO_3)_2(NO)(PPh_3)_2]$ and $[Rh(OCOCF_3)_2(NO)(PPh_3)_2]$ both showed the presence of triphenylphosphine and triphenylphosphine oxide fragmentation products in their mass spectra, however, it seems certain that the triphenylphosphine oxide is present merely as a volatile trace impurity.

Likewise the infrared data are amenable to re-interpretation. Triphenylphosphine oxide displays a strong band at 1200 cm^{-1} [ν(P=O)] that moves to lower frequency on coordination. However, the band at 1098 cm^{-1} observed in the infrared spectrum of the rhodium nitrate complex is substantially below the frequency range normally associated with the ν(P=O) vibrations in Group VIII metal triphenylphosphine oxide complexes [5], and is apparently coincident with a region in which bound triphenylphosphine and triphenylphosphine oxide both absorb strongly.

Other recent assignments of infrared bands at 1080—1100 cm^{-1} to ν(P=O) [6], though not necessarily incorrect, run counter to the weight of accumulated evidence concerning the location of this vibration for triphenylphosphine oxide complexes of the later transition elements [7, 8, 9] and should be treated with caution. Given that coordinated triphenylphosphine and triphenylphosphine oxide both absorb strongly at ca. 1100 cm^{-1}, vibrations in this vicinity do not provide a reliable means of detecting the oxidation of bound phosphine ligands.

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