Contribution from the Istituto di Chimica Generale ed Inorganica, Università di Messina, and the Cattedra di Chimica, Facoltà di Ingegneria, Università di Padova, Italy

Cationic π-Cyclopentadienyl Nitrosyl Rhodium(I) Complexes

F. Faraone, R. Pietropaolo, G. G. Troilo, and P. Piraino

Received May 4, 1973

Reactions of CpRh(CO)L (Cp = π-C_5H_5; L = PPh$_3$, PMe$_2$Ph, P(C$_6$H$_{11}$)$_3$, PEt$_2$Ph, P(n-But)$_3$) with NOPF$_6$ give cationic nitrosyl complexes [CpRh(NO)L]PF$_6$. The nature of the Rh-NO bond in these compounds is discussed considering the values of the NO stretching frequencies. By reacting the analogous Iridium(I) complex CpIr(CO)PPh$_3$ with NOPF$_6$, in methanol-benzene solution, the cation [CpIrH(CO)PPh$_3$]$^+$ is obtained.

Oxidative addition reactions on [CpRh(NO)L]$^+$ compounds are also described and the results are compared with those of analogous reactions of the CpRh(CO)PMe$_2$Ph complex. IR and ^{1}H NMR spectra are also discussed.

Introduction

There has been much interest in the reactions of nitric oxide or nitrosonium ion with transition metal complexes due to there being very different kinds of products obtainable. Furthermore, recently it has been found that transition metal-nitrosyls can act as selective homogeneous catalysts[1] and undergo reactions at the coordinated nitric oxide[2].

In this paper we report on the preparation of a new series of compounds [CpRh(NO)L]$^+$ (Cp = π-C_5H_5; L = PPh$_3$, PMe$_2$Ph, P(C$_6$H$_{11}$)$_3$, PEt$_2$Ph, P(n-But)$_3$) obtained by reacting CpRh(CO)L with NOPF$_6$. The results of some oxidative addition reactions on the cationic nitrosyl compounds are also included. Although many d^8 transition metal nitrosyl complexes have been prepared, no cyclopentadienyl rhodium or iridium nitrosyl compounds have been reported in the literature.

Experimental Section

The complexes CpM(CO)L (M = Rh, Ir) were prepared following the methods reported in the literature[3,4]. All reactions described were performed under nitrogen; all solvents were reagent grade and were dried over appropriate materials, distilled under nitrogen and degassed prior to use. Infrared spectra were recorded with a Perkin-Elmer 457 spectrophotometer. Proton N.M.R. spectra were run with a Hitachi-Perkin Elmer R20/A 60 MHz spectrometer. Melting points were determined on a Fisher-Jones hot-stage apparatus. A conductivity meter WTW LBR was used for conductivity measurements. Elemental analyses were by Bernhardt, Mülheim Germany.

π-cyclopentadienylnitrosyltriphenylphosphinerhodium (I) hexafluorophosphate, [CpRh(NO)PPh$_3$]PF$_6$. Nitrosonium hexafluorophosphate (84 mg, 0.48 mmoles), was added with vigorous stirring, to a solution of CpRh(NO)PPh$_3$ (210 mg, 0.458 mmoles) in dry benzene (10 ml) and anhydrous methanol (10 ml). The solution turns rapidly from yellow to brown-yellow and was stirred for about 15 min. The solvent was evaporated and the crude product was several times crystallized from CH$_2$Cl$_2$-ether to give yellow cristals (yield 75-80%).

The other cations of the type [CpRh(NO)L]$^+$ where L = PMe$_2$Ph, P(C$_6$H$_{11}$)$_3$, PEt$_2$Ph, P(n-But)$_3$ were all prepared in 60-70% yields in a similar fashion from the corresponding CpRh(CO)L complexes and NOPF$_6$.

Tetraphenylborate salts. The complexes [CpRh(NO)L]BPh$_4$ (L = PPh$_3$, PMe$_2$Ph, P(C$_6$H$_{11}$)$_3$) have been prepared by adding NaBPh$_4$ dissolved in methanol to a solution of [CpRh(NO)L]PF$_6$ in the same solvent. They closely resemble the corresponding hexafluorophosphate salts except for a lower solubility in organic solvents.

Reaction of CpIr(CO)PPh$_3$ with NOPF$_6$. NOPF$_6$ (58 mg, 0.34 mmoles) is added to a benzene-methanol (1:1) solution (15 ml) containing CpIr(CO)PPh$_3$ (180 mg, 0.32 mmoles). The colour of the solution turns from yellow to pale-yellow. After about 2 h the solvent was evaporated and the residue dissolved in CH$_2$Cl$_2$ and filtered. By adding ether a yellow solid

---

(1) E.A. Zucch, W.B. Hughes, D.H. Kubicek and E.T. Kittleman, *J. Amer. Chem. Soc.*, *92*, 528 (1970); G.C. Bailey, *Catal.Rev.*, *3*, 37 (1969); W.B. Hughes, *J. Amer. Chem. Soc.*, *92*, 532 (1970); J.P. Collman, N.W. Hoffman and D.E. Morris, *J. Amer. Chem. Soc.*, *91*, 5659 (1969); J. Norton, D. Valentine jr. and J.P. Collman, *J. Amer. Chem. Soc.*, *91* 7537 (1969); J.R. Norton, J.P. Collman, G. Dolcetti and W.T. Robinson, *Inorg. Chem.*, *11*, 382 (1972); J.P. Candlin and W.H. Janes, *J. Chem. Soc.*, (*C*), 1856 (1968); S.T. Wilson, and J.A. Osborn, *J. Amer. Chem. Soc.*, *93*, 3068 (1971).

(2) T.J. Meyer, J.B. Godwin and N. Winterton, *Chem. Comm.*, 872 (1970); K.R. Grundy, C.A. Reed and W.R. Roper, *Chem. Comm.*, 1501 (1970); C.A. Reed and W.R. Roper, *J. Chem. Soc.* (*A*), 3054 (1970); F. Bottomley and J.R. Crawford, *Chem. Comm*, 200 (1971); M. Foa and L. Cassar, *J. Organometal. Chem.*, *30*, 123 (1971); C.A. Reed and W.R. Roper, *J. Chem. Soc. Dalton,* 1243 (1972).

(3) H.G. Schuster-Woldan and F. Basolo, *J. Amer. Chem. Soc.*, *88*, 1657 (1966).

(4) A. J. Oliver and W.A.G. Graham, *Inorg. Chem.*, *9*, 2653 (1970).

(5) C.G. Pierpont, A. Pucci and R. Eisenberg, *J. Amer. Chem. Soc.*, *93*, 3050 (1971) and the references therein.

Table I. Analytical and physical data.

Compounds	Colour	M.p. °C	C calcd.	C found	H calcd.	H found	N calcd.	N found	Halog. calcd.	Halog. found
$[CpRh(NO)PPh_3]PF_6$	yellow	>168 dec.	45.64	45.50	3.33	3.43	2.31	2.46	18.82	18.57
$[CpRh(NO)PPh_3]BPh_4$	yellow	103-105	72.41	72.34	5.17	5.21	1.79	1.82		
$[CpRh(NO)PMe_2Ph]PF_6$	yellow	78-82	32.45	32.71	3.35	3.46	2.91	2.73	23.69	23.48
$[CpRh(NO)PMe_2Ph]BPh_4$	yellow	98-101	67.80	67.68	5.53	5.41	2.13	2.08		
$[CpRh(NO)P(C_6H_{11})_3]PF_6$	yellow	106-110	44.33	44.73	6.14	6.26	2.24	2.44	18.29	18.49
$[CpRh(NO)P(C_6H_{11})_3]BPh_4$	brown	115-119	70.77	70.45	7.33	7.20	1.75	1.84		
$[CpRh(NO)PEt_2Ph]PF_6$	brown	103-106	35.38	35.24	3.96	3.84	2.75	2.78	22.38	22.45
$[CpRh(NO)P(n\text{-}But)_3]PF_6$	brown	94-97	37.44	37.36	5.91	5.69	2.56	2.48	20.90	20.66
$CpRh(PPh_3)Cl_2$	orange	265-269	55.12	54.96	4.02	4.21			14.14	14.28
$[CpIrH(CO)PPh_3]PF_6$	yellow	85-87	41.56	41.27	3.05	3.18			16.43	16.12
$[CpIrH(CO)PPh_6]BPh_4$	white	80-81	66.43	66.22	4.76	4.81				

was obtained, which was characterized as $[CpIrH(CO)PPh_3]PF_6$.

The corresponding tetraphenylborate salt was obtained by adding $NaBPh_4$ dissolved in methanol to $[CpIrH(CO)PPh_3]PF_6$ dissolved in the same solvent.

Reactions of $[CpRh(NO)PPh_3]BPh_4$ with halogens. A CH_2Cl_2 solution of Cl_2 is added drop by drop, with stirring, to $[CpRh(NO)PPh_3]^+$ dissolved in the same solvent. The path of the reaction is followed by I.R. spectroscopy and the addition of chlorine is stopped out when the ν(NO) band at 1832 cm^{-1} disappears. The solution is then concentrated and passed through an allumina column. Using CH_2Cl_2 as eluent an orange fraction is obtained. The addition of pentane gives $CpRhPPh_3Cl_2$.

Following the same method the complexes $CpRh(PMe_2Ph)Cl_2$ and $CpRh(PMe_2Ph)Br_2$ have been obtained by reacting $[CpRh(NO)(PMe_2Ph)]^+$ with the corresponding halogens.

No reaction has been observed, in the same experimental conditions, between $[CpRh(NO)PPh_3]^+$ or $[CpRh(NO)PMe_2Ph]^+$ complexes and other halogens, alkyl or acyl halides.

Results and Discussion

On treatment of CpRh(CO)L complexes with $NOPF_6$ in dry benzene-methanol (1:1), carbon monoxide is evolved and the colour of the solution quickly turns from yellow to brown-yellow. After evaporating the solvent and crystallizing the crude products from methilene chloride-ether, new complexes $[CpRh(NO)L]PF_6$ can be obtained. The correspondent tetraphenylborate salts have been prepared, in some cases, by adding $NaBPh_4$ dissolved in methanol to a solution containing $[CpRh(NO)L]PF_6$ complexes in the same solvent.

These new complexes are yellow or brown, air-stable solids. Table I reports analytical data and some physical properties of the prepared compounds. The conductivity values in methanol or acetone are in the range expected for 1:1 electrolytes. The infrared spectra (nujol mull) of the compounds show a strong band at about 1820 cm^{-1} which can be ascribed to a ν(NO) stretching vibration.

Recent X ray diffraction studies[5] demonstrated that the NO group can be in either of two limiting oxidation states NO^+ or NO^-. Complexes containing NO^+, as a ligand, show a M-N-O angle very close to 180° and a short M-N lenght which suggests a strong π-acidity of the ligand; complexes exhibiting the NO^- form of the ligand are characterized by M-N-O angle of about 120° and longer M-N bond. The two limiting forms of the NO group cannot be unequivocally established from the ν(NO) stretching frequencies. However the ν(NO) for NO^+ are generally higher than those for NO^-. The $\nu(NO^+)$ values are between 1890 and 1600 cm^{-1} whereas values between 1700 and 1550 cm^{-1} have been reported for $\nu(NO^-)$. The stretching frequencies at about 1820 cm^{-1} for the ν(NO) found for the cationic complexes $[CpRh(NO)L]^+$, are between the highest values so far observed and bring us to the conclusion that NO is coordinated as NO^+ in these compounds. Furthermore the cationic complexes $[CpRh(NO)L]^+$ must be formally considered as nitrosyl complexes of rhodium(I) and the reaction of CpRh(CO)L with $NOPF_6$ must be regarded as a substitution reaction of CO.

In some cases the nitrosonium ion oxidatively adds to a metal complex as, for example, in the formation of $[Ir(PPh_3)_2(CO)(NO)Cl]BF_4$, obtained[6] from the reaction of the Vaska compound and $NOPF_6$, or in the case[7] of $[Ru(PPh_3)_2(NO)_2Cl]PF_6$ in which one nitrosyl coordinates as NO^+ and the other one as NO^-. The basicity of the complexes plays also an important role in the reactions with nitrosonium ion. Complexes such as $M(NO)(PPh_3)_3$ (M = Rh, Ir) and $Ir(NO)(CO)(PPh_3)_2$ react with $NOPF_6$ giving cationic $[M(NO)_2(PPh_3)_2]PF_6$ compounds but the less basic $M(NO)(PPh_3)_2I_2$ (M = Rh, Ir), in the same experimental conditions, fail to react with $NOPF_6$[8].

The tendency of CpRh(CO)L (L = tertiary phosphine) complexes to give oxidative addition reactions has been demonstrated[9-12]. In our opinion, the formation of rhodium(I) rater than rhodium(III) compounds, when $NOPF_6$ reacts with CpRh(CO)L, can be attributed to an insufficient basicity of these complexes.

---

(6) D.J. Hodgson, N.C. Payne, J.A. McGinnety, R.G. Pearson, J.A. Ibers, *J. Amer. Chem. Soc*, *90*, 4486 (1968).

(7) C.G. Pierpont, D.G. Van der Veer, W. Durland and R. Eisemberg, *J. Amer. Chem. Soc.*, *92*, 4760 (1970).

(8) G. Dolcetti, N.W. Hoffman and J.P. Collman, *Inorg. Chim. Acta*, *6*, 531 (1972).

(9) A.J. Oliver and W.A.G. Graham, *Inorg. Chem.*, 9, 243 (1970).

(10) A.J. Hart-Davis and W.A.G. Graham, *Inorg. Chem.*, 9, 2658 (1970).

(11) A.J. Hart-Davis and W.A.G. Graham, *Inorg. Chem.*, *10*, 1653 (1971).

(12) F. Faraone, C. Ferrara and E. Rotondo, *J. Organometal. Chem.*, *33*, 221 (1971).

Table II. Characteristic I.R. and N.M.R. absorptions.

Compounds	$\nu(NO)_{nujol}$	$\nu(NO)_{CH_2Cl_2}$	$\tau_{C_5H_5}$*
$[CpRh(NO)PPh_3]PF_6$	1835vs	1832vs	4.39
$[CpRh(NO)PPh_3]BPh_4$	1815vs	1825vs	
$[CpRh(NO)PMe_2Ph]PF_6$	1812vs	1828vs	4.27
$[CpRh(NO)PMe_2Ph]BPh_4$	1805vs	1825vs	
$[CpRh(NO)P(C_6H_{11})_3]PF_6$	1815vs	1820vs	4.20
$[CpRh(NO)P(C_6H_{11})_3]BPh_4$	1810vs	1818vs	
$[CpRh(NO)PEt_2Ph]PF_6$	1812vs	1822vs	4.35
$[CpRh(NO)P(n\text{-}But)_3]PF_6$	1812vs	1820vs	4.32
$CpRh(PPh_3)Cl_2$			4.75
$[CpIrH(CO)PPh_3]PF_6$	2050vs ν(CO) 2142w ν(Ir-H)		4.24
$[CpIrH(NO)PPh_3]BPh_6$	2048vs ν(CO) 2140w ν(Ir-H)		

* In $CDCl_3$ solution.

Table 2 reports I.R. and N.M.R. data for the prepared compounds. The dominant features of the I.R. spectra are, besides the strong ν(NO) band at about 1820 cm^{-1}, the characteristic bands of PF_6^- (835 vs and 560 s cm^{-1}) or BPh_4^- and those of the phosphine ligands. In the case in which the anion is not PF_6^- it is possible to assign also the band at about 830 cm^{-1} to the out-of-plane deformation of the π-cyclopentadienyl. No NO_3^- or NO_2^- absorptions in the 900-1460 cm^{-1} region have been observed. The ^1H N.M.R. spectrum shows for all the $[CpRh(NO)L]^+$ complexes an absorption centered at about 4.25 τ. The cyclopentadienyl resonances are expected to be split by rhodium (^{103}Rh 100% abundance, spin½) and by phosphorus when the latter is present. This feature is sometimes observed, but in some cases as with $[CpRh(NO)L]^+$ complexes the couplings seem to be beyond the resolution of the spectrophotometer. The N.M.R. spectrum of the complex $[CpRh(NO)PMe_2Ph]PF_6$ shows a doublet centered at 7.80 τ (J = 13.2 cps) attributable to methyl resonances. The $[CpRh(NO)L]BPh_4$ compounds are not soluble in $CDCl_3$ to allow N.M.R. spectra to be run.

$CpIr(CO)PPh_3$ reacts in 1:1 benzene-methanol solution with $NOPF_6$ giving the cationic $[CpIrH(CO)PPh_3]PF_6$ complex. The corresponding tetraphenylborate salt[4] can be obtained by adding $NaBPh_4$ dissolved in methanol to a solution containing $[CpIrH(CO)PPh_3]PF_6$ in the same solvent. The I.R. spectrum of $[CpIrH(CO)PPh_3]^+$ shows a very strong ν (CO) at 2050 cm^{-1} and a weak band at 2140 cm^{-1} due to the ν (Ir-H) stretching vibration. Other cases in which protonated species are obtained by reacting $NOPF_6$ with d^8 metal complexes in methanol solutions have been reported[13] and the species HPF_6, formed from the reaction of $NOPF_5$ with CH_3OH, is thought to be responsible for such a behaviour. The easy formation of $[CpIrH(CO)PPh_3]^+$, on the other hand, accords with the basic character of $CpIr(CO)PPh_3$ being stronger than that of $CpRh(CO)PPh_3$. Similarly it has been reported[13] that *trans*-$Fe(CO)_3(PPh_3)_2$ reacts with NOY (Y = BF_4 or PF_6) giving $[Fe(CO)_2NO(PPh_3)_2]$ Y, whereas the analogous but more basic complexes $M(CO)_3(PPh_3)_2$ (M = Ru, Os) give protonated species $[MH(CO)_3(PPh_3)_2]^+$.

Oxidative addition reactions. The ability of $[CpRh(NO)L]^+$ complexes to react in oxidative additions is very limited. The neutral $CpRh(CO)PM_2Ph$ compound oxidatively adds[9-12] CH_3I, CH_3COBr, CF_3COCl, $C_6H_5CH_2X$, $ClCH_2CN$, halogens whereas $[CpRh(NO)PPh_3]^+$, at room temperature, reacts only with Cl_2 giving $CpRhPPh_3Cl_2$, but no reaction has been observed with Br_2, I_2, CH_3I,$ClCH_2CN$. The replacement of PPh_3 with the more basic phosphine PMe_2Ph does not change substanzially the oxidative ability of these types of complexes. $[CpRh(NO)PMe_2Ph]^+$ reacts in fact with Cl_2 and Br_2 giving the previously known[9] complexes $CpRh(PMe_2Ph)Cl_2$ and $CpRh(PMe_2Ph)Br_2$, but no other oxidative addition reactions have been observed.

Kinetic studies[10,11] have already demonstrated that CpRh(CO)L complexes react with alkyl iodides, benzyl and allyl halides following a mechanism in which the rate determining step is a nucleophilic attack by the metal atom on the carbon of the organic molecule. The same behaviour was confirmed[11] in the reaction of analogous compounds of cobalt(I) and iridium(I) and CH_3I or C_2H_5I. In the last case cationic iridium(III) alkyl complexes can be isolated at room temperature. Furthermore complexes such as $[CpRh(CO)(PMe_2Ph)Cl]Cl$ and $[CpRh(CO)(PMe_2Ph)Br]Br$ have been obtained at low temperatures by reacting $CpRh(CO)PMe_2Ph$ respectively with Cl_2 and Br_2 and isolated as tetraphenylborate salts. The behaviour of $[CpRh(NO)L]^+$ compounds in the oxidative addition reactions clearly demonstrates that these complexes are weaker bases than the analogous CpRh(CO)L and the nucleophylic attack of the metalic center on the oxidant molecule is not favoured. The presence of the coordinated ligand NO, which is a stronger π-acid than CO, and the positive charge on the complex must be responsible for such a behaviour.

On the other hand, an inferior ability of d^8 cationic complexes to give oxidative additions, in relation to neutral complexes, has been demonstrated in several cases.

Acknowledgments. The authors thank C.N.R. for financial support.

---

(13) B.F.G. Johnson and J.A. Segal, *J. Organometal. Chem.*, 31, C 79 (1971).