Inorganica Chimica Acta, 30 (1978) 119–126

Oxidative Addition of Nitrogen(IV) Oxide to Complexes of Platinum, Iridium, and Rhodium

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Received January 26, 1978

Nitrogen(IV) oxide oxidatively adds to $[Pt(PPh_3)_2(C_2H_4)]$ to give $[Pt(PPh_3)_2(NO)(NO_3)]$, a nitrosyl platinum complex, which reacts rapidly with dioxygen to give cis-$[Pt(PPh_3)_2(NO_3)_2]$. *The nitrato–nitro complex $[Ir(PPh_3)_2(CO)Cl(NO_3)(NO_2)]$ is formed in the reactions of N_2O_4 with* trans-$[Ir(PPh_3)_2(CO)Cl]$ *and with $[Ir(PPh_3)_2(CO)(NO)Cl]BF_4$. Nitrato–nitro iridium(III) complexes are formed in the reactions of N_2O_4 with $[Ir(PMePh_2)_2(CO)Cl]$, $[Ir(PPh_3)_3(CO)H]$, $[Ir(PPh_3)_2(CO)_3]BPh_4$, and $[Ir(PPh_3)_2(CO)(NO)]$, but reaction of N_2O_4 with $[Ir(Ph_2PCH_2CH_2PPh_2)_2]Cl$ gives the dinitro complex $[Ir(Ph_2PCH_2CH_2PPh_2)_2(NO_2)_2]Cl$. Reaction of N_2O_4 with* trans-$[Rh(PPh_3)_2(CO)Cl]$ *in the solid state or in toluene gives NO, CO_2, and $[Rh_2(PPh_3)_4(NO_3)_3(NO_2)_2Cl]$. In dichloromethane, this latter reaction gives $[Rh(PPh_3)_2(NO_3)Cl_2]\cdot CH_2Cl_2$. Formation of this nitrato complex was also demonstrated in the reaction of N_2O_4 with $[Rh(PPh_3)_2Cl_2(NO)]$ and in the photochemical reaction of dioxygen and $[Rh(PPh_3)_2Cl_2(NO)]$. Nitrosyl tetrafluoroborate reacts with* trans-$[Rh(PPh_3)_2(CO)Cl]$ *to give $[Rh(PPh_3)_2(CO)(NO)Cl]BF_4$, which in the presence of chloride ion gives $[Rh(PPh_3)_2(NO)Cl_2]$.*

Introduction

Complexes of metals with d^8 and d^{10} electronic configuration undergo oxidative addition reactions with compounds such as halogens, acids, alkyl, acyl, and sulfonyl halides, and dioxygen to form complexes of metals with d^6 and d^8 electronic configuration [1]. These reactions may proceed by a single two-electron pathway in which the metal as a nucleophile attacks a substrate [2], or by successive one electron radical addition steps [3]. The reactions of the radical nitrogen(II) oxide(NO·) with complexes of d^{10} and d^8 metals are complex [4] and even greater complexity might be expected for reactions of nitrogen(IV) oxide for which the $NO_2\cdot$, NO·, and $NO_3\cdot$ radicals and ionic and molecular species NO^+, NO_3^- and N_2O_4 may be viable reactive entities. The recent demonstration of the oxidative addition of two $(CF_3)_2NO$ radicals per metal atom to complexes of d^8 and d^{10} metals [5] raises the possibility that direct addition of $NO_2\cdot$, NO· or $NO_3\cdot$ radicals which are good ligands may be detected in intermediates or in isolable products to elucidate the course of reactions of nitrogen (IV) oxide. The reactions of N_2O_4 with complexes of metals containing carbonyl and organophosphine ligands have not been extensively investigated. In reactions with metal complexes such as $[Mo(CO)_2(Ph_2PC_2H_4PPh_2)_2]$ [6], and $[Fe(S_2CNEt_2)_2NO]$ [7] which readily undergo one electron oxidation, nitrogen(IV) oxide is typically a one electron oxidant. Reactions of N_2O_4 with methylated platinum(II) and gold(III) complexes have been briefly described [8], but the course of these reactions has not been fully elucidated. The reactivity pattern for the formation of nitrato complexes from the reactions of N_2O_4 and metal–dioxygen complexes is well established [9]. Reactions of N_2O_4 with complexes of d^8 and d^{10} metals may be relevant to recent investigations of the catalysis of the ecologically significant reaction of CO and NO [10], since NO in the presence of O_2 is rapidly converted to N_2O_4. The purpose of this investigation is to seek to establish the reactivity pattern for the reactions of nitrogen(IV) oxide with complexes of the d^8 and d^{10} metals.

Experimental

The complexes $[Pt(PPh_3)_2(C_2H_4)]$ [11], $[Pt(PPh_3)_3]$ [12], $[Ir(PPh_3)_2(CO)Cl]$ [13], $[Ir(PMePh_2)_2(CO)Cl]$ [14], $[Ir(PPh_3)_2(CO)Cl(NO)]BF_4$ [15], $[Ir(PPh_3)_3(CO)H]$, $[Ir(PPh_3)_2(CO)(NO)]$ [16], $[Ir(Ph_2PC_2H_4PPh_2)_2]Cl$ [17], and $[Rh(PPh_3)_2(CO)Cl]$ [13] were prepared by literature methods. Nitrogen(IV) oxide (Matheson Research Grade) was redistilled several times on a vacuum system to remove NO and O_2 and protected from light. All solvents for the d^8 and d^{10} complexes were degassed

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0020-1693/78/0030-0119$2.25

Printed in Switzerland

TABLE I. Infrared Spectral Data (cm^{-1}).

	$\nu(NO_3)$			$\nu(NO_2)$		Other
$[Pt(PPh_3)_2(NO_3)_2$	1495s	1270vs	970s			1650 (NO)
$[Pt(PPh_3)_2(NO)(NO_3)]$	1495	1265vs, 1270sh	980m			
$[Pt(PPh_3)_2(NO_2)_2]$				1420, 1330	820	
$[Ir(PPh_3)_2(CO)(NO_2)(NO_3)Cl]$	1520	1270	970m	1435, 1310	822	2085 (CO)
$[Ir(PMePh_2)(CO)(NO_2)(NO_3)Cl]$	1500m	1260s	970m	1410, 1305	825	2050 (CO)
$[Ir(PPh_3)_2(CO)H(NO_2)(NO_3)]$	1515	1275	960	1410, 1340	825	2150 (Ir–H) 2045 (CO)
$[Ir(PPh_3)_2(NO)(NO_2)(NO_3)]$	1505	1270	980, 970	1410, 1335	828	1570 (NO)
$[Ir(Ph_2PC_2H_4PPh_2)_2(NO_2)_2]Cl$				1340	835	
$[Ir(PPh_3)_2(CO)(NO_2)(NO_3)_2]$	1520	1260	970	1435, 1325	828	2080 (CO)
$[Rh_2(PPh_3)_4(NO_3)_3(NO_2)_2Cl]$	1555, 1535	1380	980	1460, 1300	815	
$[Rh(PPh_3)_2(NO_3)Cl_2]$	1510, 1380	1230	995			

by freeze-thaw methods. Infrared spectra were recorded on Perkin-Elmer Model 621 or 137B spectrophotometers and are reported in Table I. Only frequencies other than those due to the PPh_3 ligand are listed in this paper. Proton nmr spectra were obtained on a Varian A60 spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Decomposition temperatures (listed as mp) were obtained using a Mel-Temp apparatus and are uncorrected. Thin-layer chromatography was performed with Brinkmann Instruments Polygram SIL N-HR/UV using 4:1:1 C_6H_6:CH_3OH:CH_2Cl_2. Columns containing molecular sieves 5A and Poropak Q were used for gas chromatographic analysis of CO–NO and N_2O–CO_2 respectively.

Reaction of N_2O_4 with $[Pt(PPh_3)_3]$

A sample of 247 mg of solid $[Pt(PPh_3)_3]$ was treated with N_2O_4 (1 atm) for 15 hr. In addition to ir bands of the final product, the spectrum of the pale yellow solid had bands at 1190 and 720 cm^{-1} due to Ph_3PO. The product was dried in vacuo, and recrystallization from CH_2Cl_2–CH_3OH gave colorless crystals (102 mg, 88%). *Anal.* Calcd for $[Pt(PPh_3)_2(NO_3)_2]\cdot 1/2CH_2Cl_2$: C, 49.2; H, 3.44; N, 3.04. Found C, 48.6; H, 3.50; N, 3.04. The presence of the dichloromethane was confirmed by the nmr spectrum.

Reaction of N_2O_4 with $[Pt(PPh_3)_2(C_2H_4)]$

Toluene (10 ml) was frozen on a sample of 205 mg $[Pt(PPh_3)_2(C_2H_4)]$ in a vacuum system. Nitrogen(IV) oxide was then introduced and frozen on the sample. The reaction mixture was warmed to 0 °C and allowed to react for 15 min. Analysis of the gas above the reaction mixture by gas chromatography and ir indicated the absence of NO or N_2O. The nitrogen(IV) oxide and toluene were removed from the reaction mixture by vacuum transfer, leaving a pale yellow product which was reactive with air and with the KBr windows used for ir sampling. *Anal.* Calcd for $[Pt(PPh_3)_2(NO)(NO_3)]$: C, 53.2; H, 3.72; N, 3.45. Found: C, 52.2; H, 3.78; N, 3.50.

Recrystallization of this compound in air from dichloromethane–methanol afforded colorless crystals (47%); Mp 228.5–229.3 °C (decomp). *Anal.* Calcd. for $[Pt(PPh_3)_2(NO_3)_2]\cdot 1/2CH_2Cl_2$: C, 49.18; H, 3.44; N, 3.04. Found: C, 49.53; H, 3.60; N, 3.09. The presence of the dichloromethane solvent was demonstrated by the nmr spectrum.

A solution of 97 mg of $[Pt(PPh_3)_2(NO)(NO_3)]$ in 16 ml dichloromethane under 20 psi CO was stirred for 24 hr. The solvent was removed under reduced pressure. The product was washed with ether and recrystallized from CH_2Cl_2–Et_2O as 20 mg (21%) of colorless microcrystals. Mp 261–263 °C. Ir: (Nujol) (NO_2) 1410, 1338, 825 cm^{-1} identical with spectra of the product $[Pt(PPh_3)_2(NO_2)_2]$ obtained from the reaction of $[Pt(PPh_3)_2Cl_2]$ and KNO_2. A solution of $[Pt(PPh_3)_2(NO)(NO_3)]$ in dichloromethane under argon was stirred for 1 hour. Only a slight decrease in the $\nu(NO)$ band at 1650 cm^{-1} and low intensity of nitro vibrations at 1338 and 825 cm^{-1} were noted.

Reaction of N_2O_4 with trans-*$[Ir(PPh_3)_2(CO)Cl]$*

A sample of 85 mg of *trans*-$[Ir(PPh_3)_2(CO)Cl]$ was allowed to react with 740 mm of N_2O_4 for 5 hr. The resulting colorless solid was dried in vacuo at 58 °C. *Anal.* Calcd for $[Ir(PPh_3)_2(CO)Cl(NO_2)(NO_3)]$: C, 50.03; H, 3.40; N, 3.15. Found: C, 49.96; H, 3.38; N, 3.12. Mp 205–212 °C (with decomp.). Ir (Nujol): 2085 vs, 2080 sh, 1520 s, 1435 s, 1310 s, 1270 s, 970 m, 822 s. Reaction of N_2O_4 with solutions of *trans*-$[Ir(PPh_3)_2(CO)Cl]$ in dichloromethane or in toluene at 0 °C or in liquid N_2O_4 gave the same product Thin layer chromatography indicated the formation of a single product in this reaction The formation of nitric oxide by-product was shown by gas chromatography on a molecular sieves VA column

A solution of 309 mg of *trans*-$[Ir(PPh_3)_2(CO)Cl]$ in 45 ml toluene was heated at refluxing temperature and an excess of nitrogen dioxide was introduced The solution immediately turned brown After 10 min the solvent was evaporated under reduced pressure and the remaining solid was washed with ether, and then with 5 ml dichloromethane The gray solid (Mp dec 217–220 °) has ir bands at 2080 vs, 1570 w, 1305 vs, and 820 cm^{-1} The relative intensity of the ir bands due to the nitro ligand (1305 and 820 cm^{-1}) are considerably enhanced compared to the ir bands of the nitrato ligand at 1520, 1270 and 970 cm^{-1} Addition of 20 ml methanol to the dichloromethane wash solution gave an off-white solid (Mp 205–206° dec) which has an ir spectrum identical with $[Ir(PPh_3)_2(CO)(NO_3)(NO_2)Cl]$

Nitrogen(IV) oxide was frozen on a solution of 235 mg of *trans*-$[Ir(PMePh_2)_2(CO)Cl]$ in 6 ml toluene The mixture was allowed to warm to 0 °C and maintained at this temperature for 10 min before the solvent was removed in vacuo The product was washed with ether and recrystallized from CH_2Cl_2–MeOH as a pink-orange solid Yield 81 mg (30%) Mp 163–165 °C *Anal* Calcd for $[Ir(PMePh_2)_2(CO)Cl(NO_3)(NO_2)]$ C, 42 44, H, 3 43, N, 3 67 Found C, 42 63, H, 3 60, N, 3 41 Ir (Nujol) (CO) 2050 s, (NO_3) 1510 sh, 1500 m, 1260 s, 970 m, (NO_2) 1410 s, 1305 s, 825 s cm^{-1}

Reaction with $[Ir(PPh_3)_2Cl(CO)(NO)]BF_4$

The addition of N_2O_4 to a solution of 148 mg $[Ir(PPh_3)_2Cl(CO)(NO)]BF_4$ in 15 ml CH_2Cl_2 resulted in a color change from violet to green The solution was stirred for 2 hours and the excess N_2O_4 was removed with a stream of N_2 The pale yellow solution was filtered and reduced in volume Addition of methanol afforded 75 mg of a colorless solid with spectrum identical to that of $[Ir(PPh_3)_2(CO)(NO_3)(NO_2)Cl]$

Reaction with $[Ir(PPh_3)_3(CO)H]$

Benzene (7 ml) was transferred in a vacuum system to 204 mg of $[Ir(PPh_3)_3(CO)H]$ and an excess of N_2O_4 was frozen on the benzene Upon warming to 6 °C the yellow solid became tan in color and the solution green Examination of the gas above the reaction mixture by gas chromatography indicated the presence of nitric oxide The nitrogen(IV) oxide and benzene were removed *in vacuo* and the off white solid was washed with ether, and then recrystallized from dichloromethane–ether as off-white crystals Yield 146 mg (82%) Mp 126–130 °C (decomp) *Anal* Calcd for $[Ir(PPh_3)_2(CO)H(NO_2)(NO_3)]$ C, 52 0, H, 3 66, N, 3 28 Found C, 51 9, H, 3 71, N, 3 19 Ir (Nujol) (Ir–H) 2150 m, (CO) 2080 w, 2045 m, (NO_3) 1515 s, 1275 m, 1260, 980 w, 960 s, (NO_2) 1410 s, 1340 s, 825 m cm^{-1}

The reaction of gaseous N_2O_4 with solid $[Ir(PPh_3)_3(CO)H]$ gave a product which had the same ir spectrum as the product above

Reaction with $[Ir(CO)(NO)(PPh_3)_2]$

An excess of N_2O_4 was frozen on a solution of 162 mg of $[Ir(PPh_3)_2(CO)(NO)]$ in 7 ml toluene and the reaction mixture was warmed to 0 °C The solution turned green and gas evolution was noted The reaction was allowed to react at 0 °C for 20 min Gas chromatographic analysis showed the formation of CO_2 and N_2O, as well as NO and CO The cream-colored solid was washed with Et_2O and dried *in vacuo* Thin layer chromatography revealed the presence of 3 major species Ir (Nujol) (CO) 2110 m, 2090 m, (NO) 1575 s, (NO_3) 1540 s, 1520 s, 1275, 982 m, (NO_2) 1325, 825 m When the cream-colored solid was washed with CH_2Cl_2, a white solid (Mp 225–226°) (47 mg) was isolated *Anal* Calcd for $[Ir(PPh_3)_2(NO)(NO_2)(NO_3)]\cdot CH_2Cl_2$ C, 47 3. H, 3 43, N, 4 47 Found C, 48 3, H, 3 74, N, 4 42 Ir (Nujol) (N–O) 1570, (NO_3) 1505 m, 1270, 980 m, 970 m, (NO_2) 1410 m, 1335 s, 828 m The CH_2Cl_2 wash solution was evaporated and thin layer chromatography (C_6H_6–MeOH–CH_2Cl_2, 4 1 1) showed the presence of 2 species

Reaction with $[Ir(Ph_2PCH_2CH_2PPh_2)_2]Cl$

An excess of N_2O_4 was frozen on a solution of 91 mg of $[Ir(Ph_2PCH_2CH_2PPh_2)_2]Cl$ in 7 ml $CHCl_3$ The mixture was warmed to 0 °C and allowed to react for 15 min before the N_2O_4 and $CHCl_3$ were removed *in vacuo* The red-brown residue was recrystallized from CH_2Cl_2–Et_2O to give an off-white solid (71 mg, 72%) Mp 209–212° Ir (Nujol) (NO_2) 1340 vs, 835 m, cm^{-1} *Anal* Calcd for $[Ir(Ph_2PC_2H_4PPh_2)_2(NO_2)_2]Cl\cdot 2CH_2Cl_2$ C, 50 4, H, 4 07, N, 2 17 Found C, 50 5, H, 4 37, N, 2 75 A sample of solid $[Ir(Ph_2PC_2H_4PPh_2)_2]Cl$ (103 mg) was treated at 78 °C with NO_2 gas for 10 min Chromatographic analysis of the gas showed the absence of nitric oxide The ir spectrum of the solid (1335 s, 830 m cm^{-1}) indicated the formation of the dinitro complex but thin layer chromatography revealed a significant amount of unreacted starting reagent The reaction of N_2O_4 with $[Ir(Ph_2PC_2H_4PPh_2)_2]Cl$ in methanol at 25 °C gave a tan product which was shown by thin layer chromatography to consist of at least three products which could not be completely separated from each other The predominant product has ir bands at 1330–1350 vs and 825 m cm^{-1} characteristic of the dinitro complex

Reaction with $[Ir(PPh_3)_2(CO)_3]BPh_4$

When N_2O_4 was condensed on a sample of 103 mg of $[Ir(PPh_3)_2(CO)_3]BPh_4$, a dark green solution was immediately formed. Gas chromatographic analysis showed that CO and NO were evolved. After allowing the reaction to proceed for 10 min, the solvent was stripped and the sample was dried *in vacuo* for 20 min. Recrystallization from CH_2Cl_2–Et_2O gave 59 mg of a tan product. Mp. 213–215°. *Anal.* Calcd for $[Ir(PPh_3)_2(CO)(NO_3)_2(NO_2)]\cdot 5/4CH_2Cl_2$: C, 45.0; H, 3.21; N, 4.12. Found: C, 44.5; H, 3.41; N, 4.30. Ir (Nujol): (CO) 2080 s; (NO_3) 1520, 1260, 970; and (NO_2) 1435, 1325, 828 cm^{-1}.

Reaction of N_2O_4 *with* trans-$[Rh(PPh_3)_2(CO)Cl]$

A sample of solid *trans*-$[Rh(PPh_3)_2(CO)Cl]$ (101 mg) in a 50 ml flask charged with 1 atm of N_2O_4 was allowed to react for 96 hr. The reaction flask was replenished twice with a fresh charge of N_2O_4. An ir spectral study revealed that the orange–brown product had a medium intensity band at 2090 cm^{-1}, in addition to bands in the final product. The product was dried *in vacuo* at 58 °C for 15 hr. The 2090 cm^{-1} band was not present in the dried product. *Anal.* Calcd for $[Rh_2(PPh_3)_4(NO_3)_3(NO_2)_2Cl]$: C, 55.1 H, 3.85; N, 4.45; Cl, 2.26. Found: C, 55.0; H, 4.03; N, 4.55; Cl, 2.88. Mp 185–187 °C (decomp). Ir(KBr): 1555 vs, 1535 vs, 1460 m, 1380 s, 1300 vs, 1150 w, 980 s, 815 s. The product (90 mg) is insoluble in methanol and acetone, but slightly soluble in benzene and chloroform.

A suspension of 1.02 g of *trans*$[Rh(PPh_3)_2(CO)Cl]$ in 15 ml dichloromethane treated with N_2O_4 initially gave a green solution and a yellow solid, which dissolved to give a brown solution. Methanol (5 ml) was added to precipitate 130 mg of a yellow solid which was dried *in vacuo*. This product had an ir spectrum which was identical to the product above. Found: C, 54.2; H, 4.03; N, 4.95; Cl, 2.75.

Nitrogen(IV) oxide was frozen on 265 mg of *trans*-$[Rh(PPh_3)_2(CO)Cl]$ and 4 ml toluene. The sample was warmed to 0 °C to give a green solution and a green solid. This green product was dried *in vacuo*. Mp. 189–190 °C. Ir (Nujol): 2080 w (CO). 1640 m (NO), 1560, 1510, 1280, 980 (NO_3); 1310, 825 (NO_2). Thin layer chromatography indicated a single component. The green solid warmed to 80 °C in toluene became yellow and the yellow product which was isolated does not have the 2080 and 1640 cm^{-1} bands, but has an ir spectrum identical to that of $[Rh_2(PPh_3)_2(NO_3)_3(NO_2)_2Cl]$. *Anal.* Found: C, 56.5; H, 4.18; N, 4.13; Cl, 2.74.

A solution of 112 mg of *trans*-$[Rh(PPh_3)_2(CO)Cl]$ in 10 ml dichloromethane was stirred under 1 atm of N_2O_4 for 20 min. The solvent was stripped from the dark orange solution. Trituration of the solid with ether gave an orange powder (104 mg), which was refluxed in CH_2Cl_2 for 3 hr. Addition of methanol gave 44 mg of bright orange crystals, which were recrystallized from CH_2Cl_2–CH_3OH. *Anal.* Calcd for $[Rh(PPh_3)_2Cl_2(NO_3)\cdot 3/4\ CH_2Cl_2]$: C, 53.8; H, 3.87; N, 1.71; Cl, 15.2. Found: C, 53.5; H, 3.54; N, 1.44; Cl, 15.3. Ir (KBr): 1510 vs, 1380 m, 1230 s, 1160 w, 995 m, 525 s. Mp. 160 °C (decomp to orange powder). The powder does not react with dioxygen.

Reactions of $[Rh(PPh_3)_2X_2(NO)]$

A suspension of 131 mg of $[Rh(PPh_3)_2Cl_2(NO)]$ in 10 ml CH_2Cl_2 was treated with a stream of nitric oxide which gave a bright orange solution. The solvent was removed *in vacuo* and the orange solid washed with ether. Recrystallization from dichloromethane–methanol afforded orange crystals. *Anal.* Calcd for $[Rh(PPh_3)_2Cl_2NO_3\cdot 3/4CH_2Cl_2]$: C, 53.8; H, 3.87; N, 1.71. Found: C, 53.8; H, 3.80; N, 1.76.

A suspension of 262 mg of $[Rh(PPh_3)_2Cl_2(NO)]$ in 5 ml CH_2Cl_2 treated with N_2O_4 gave a red solution. After removal of 3 ml of solvent, 147 mg of an orange–red solid was recovered by filtration; addition of 10 ml of methanol to the filtrate gave an additional 50 mg of product which had an ir spectrum identical to that of $[Rh(PPh_3)_2Cl_2(NO_3)]\cdot 3/4CH_2Cl_2]$.

A suspension of 68 mg of $[Rh(PPh_3)_2Br_2NO]$ in 10 ml CH_2Cl_2 was stirred under 1 atm of NO_2 for 20 min. The reactant completely dissolved and the solvent was stripped *in vacuo*. After washing with ether and drying *in vacuo* the orange product $[Rh(PPh_3)_2Br_2NO_3]$ (58 mg) had an ir spectrum like that of the corresponding chloro complex. Ir (KBr): 1555 vs, 1540 s, 1430 s, 1380 m, 1305 vs, 990 m, 820 cm^{-1}.

A solution of 364 mg of $[Rh(PPh_3)_2Cl_2NO]$ in 40 ml of CH_2Cl_2 under 1 atm of dioxygen was photolyzed at 350 nm for 18 hours. The dichloromethane was distilled under reduced pressure to 10 ml and 10 ml hexane was added. The brown product (292 mg) had a very intense infrared absorption band at 1515 cm^{-1} characteristic of $[Rh(PPh_3)_2Cl_2NO_3]$.

Reaction of trans-$[Rh(PPh_3)_2(CO)Cl]$ *with* $NOBF_4$

The addition of 511 mg of $NOBF_4$ to a yellow solution of 1.04 g of *trans*-$[Rh(PPh_3)_2(CO)Cl]$ in $CHCl_3$ led to a change in color from yellow, to brown, and to green. The ir spectrum of this solution has a very intense band at 2090 cm^{-1} (CO) and bands at 1775, 1730 cm^{-1} (NO). Addition of a solution of 266 mg LiCl in 10 ml ethanol gave vigorous gas evolution with concomitant color change to red and formation of a brown precipitate which was recrystallized from dichloromethane. Yield: 917 mg (84%). *Anal.* Calcd for $[Rh(PPh_3)_2Cl_2(NO)]$: C, 59.36; H, 4.15; N, 1.92; Cl, 9.84. Found: C, 59.25; H, 4.09; N, 1.89; Cl, 9.95.

Results and Discussion

Platinum Complexes

The solid product resulting from the reaction of solid $[Pt(PPh_3)_3]$ and gaseous nitrogen (IV) oxide at 25 °C has an infrared spectrum which indicates the presence of Ph_3PO and *cis*-$[Pt(PPh_3)_2(NO_3)_2]$ (2). This latter complex (as a solvate) was isolated and characterized by elemental analysis and ir spectroscopy: Nitrato bands [18] (Table I) were observed in Nujol at 1495, 1270 and 970 cm^{-1} and a sharp strong band was found at 545 cm^{-1} which is observed in the spectra of *cis* Pt-PPh_3 complexes [19]. The spectrum of complex 2 was identical to that for $[Pt(PPh_3)_2(NO_3)_2]$ obtained from the reaction of N_2O_4 and $[Pt(PPh_3)_2O_2]$ [9b]. The ir spectrum of $[Pt(PPh_3)_2(NO_3)_2]$ in KBr had a new band at 1370 cm^{-1} which is due to ionic nitrate resulting from the metathetical displacement in the KBr matrix. In our initial trials for the reaction of N_2O_4 and $[Pt(PPh_3)_2C_2H_4]$ the product obtained was $[Pt(PPh_3)_2(NO_3)_2]$. A careful assay by ir spectroscopy and gas chromatography, however, showed no evidence for the formation of nitric oxide and other lower valent nitrogen oxides which would be expected in the stoichiometric reaction of N_2O_4 leading to the dinitrato complex. A subsequent careful study of the reaction of N_2O_4 with $[Pt(PPh_3)_2C_2H_4]$ in toluene at 0 °C led to the isolation and characterization of $[Pt(PPh_3)_2(NO)(NO_3)]$ (1).

$$[Pt(PPh_3)_2C_2H_4] + N_2O_4 \longrightarrow \underset{\mathbf{1}}{[Pt(PPh_3)_2(NO)(NO_3)]} \xrightarrow{O_2} \underset{\mathbf{2}}{[Pt(PPh_3)_2(NO_3)_2]} \qquad (1)$$

A coordinated nitrato ligand in **1** is indicated by ir bands at 1495, 1265, and 980 cm^{-1} and the coordinated nitrosyl ligand by an ir absorption band at 1650 cm^{-1}. Complex **1** (even in the solid state) was found to be extremely reactive with dioxygen with disappearance of the ν(NO) band at 1650 cm^{-1} and enhancement of intensity of the nitrato ir bands. This reaction of the nitrosyl complex with dioxygen to form a nitrato complex resembles the reactivity pattern observed in the reactions of complexes containing bent Ir–N–O bonds with dioxygen to form nitrato complexes [20]. The formation of $[Pt(PPh_3)_2(NO)(NO_3)]$ by the reaction of NO_2 with $[Pt(PPh_3)_4]$ was briefly mentioned [21], but details of its characterization were not presented. It is likely that this same complex is initially formed in reactions of NO_2 with $[Pt(PPh_3)_3]$, but subsequent reaction with dioxygen gives the dinitrato complex described above. Organophosphine complexes of platinum containing the nitrosyl ligand are rare [22]. Square planar metal nitrosyl complexes have not previously been discovered, but Haymore and Ibers [23] proposed that a likely candidate for such a complex would be *trans*-$[PtX(NO)(PR_3)_2]$. The reactivity with dioxygen and a sharp strong ir band at 550 cm^{-1} in the spectrum of **1** indicative of a *cis* structure in planar platinum(II) complexes provide strong support for the suggestion that the complex $[Pt(PPh_3)_2(NO)(NO_3)]$ isolated in this study is a square planar platinum(II) complex with a NO^- ligand and a bent Pt–N–O bond, rather than a tetrahedral Pt(0) complex with a linear Pt–N–O bond. Crystals suitable for X-ray crystallographic confirmation of this suggestion have not yet been obtained.

A solution of $[Pt(PPh_3)_2(NO)(NO_3)]$ in CH_2Cl_2 under CO was found to give *cis*-$[Pt(PPh_3)_2(NO_2)_2]$ presumably resulting from oxygen atom transfer from the nitrato to nitrosyl ligand. A differential scanning calorimetric study indicated that the oxygen atom transfer process is not facile in the solid state and that slow decomposition of the compound takes place instead.

Iridium Complexes

Reaction of gaseous or liquid nitrogen(IV) oxide with solid *trans*-$[Ir(PPh_3)_2(CO)Cl]$ and the reaction of N_2O_4 with solutions of *trans*-$[Ir(PPh_3)_2(CO)Cl]$ in dichloromethane, chloroform, benzene or toluene give nitric oxide and the colorless nitrato–nitro complex $[Ir(PPh_3)_2(CO)Cl(NO_3)(NO_2)]$.

$$\textit{trans}\text{-}[Ir(PPh_3)_2(CO)Cl] + 3\,NO_2 \rightarrow [Ir(PPh_3)_2(CO)Cl(NO_2)(NO_3)] + NO \qquad (2)$$

This iridium(III) carbonyl has ν(CO) at 2085 cm^{-1} compared to the ν(CO) at 1960 cm^{-1} in the Ir(I) starting material. The nitrato ligand is characterized by ir absorption [18] bands at 1520, 1270, and 970 cm^{-1} and the nitro [18] ligand by absorption at 1435, 1310 and 822 cm^{-1}. Since the concentration of NO_2 monomer relative to the N_2O_4 dimer increases with temperature, the reaction of nitrogen-(IV) oxide with $[Ir(PPh_3)_2(CO)Cl]$ in refluxing toluene was investigated to determine whether a new product would be formed. The product isolated had intense bands which may be attributed to $[Ir(PPh_3)_2(CO)Cl(NO_2)_2]$ (ir absorption at 1305 and 820 cm^{-1}) but this compound could not be separated cleanly from $[Ir(PPh_3)_2(CO)Cl(NO_3)(NO_2)]$ which was also formed. The reaction of N_2O_4 and *trans*-$[Ir(PMePh_2)_2(CO)Cl]$ also gives a nitro-nitrato compound $[Ir(PMePh_2)_2(CO)Cl(NO_2)(NO_3)]$.

The reaction of nitrogen(IV) oxide with $[Ir(PPh_3)_3(CO)H]$ gives the hydrido-nitrato-nitro carbonyl iridium(III) complex $[Ir(PPh_3)_2(CO)H(NO_2)(NO_3)]$. The ir data: ν(Ir–H) 2150 cm^{-1}, ν(CO) at 2045 cm^{-1} and nitrato–nitro absorptions shown in Table I fully support the formulation. Reaction of N_2O_4 with the d^{10} complex $[Ir(CO)(NO)(PPh_3)_2]$ resulted in the formation of a nitrato–nitro iridium-

(III) carbonyl nitrosyl complex with ν(CO) at 2110, 2090 cm^{-1} and ν(NO) at 1575 cm^{-1}, but the reaction also gave two additional products which were difficult to separate from the major species

Unlike the reactions with all the other complexes of iridium investigated, the reaction of N_2O_4 with the cationic complex $[Ir(Ph_2PC_2H_4PPh_2)_2]Cl$ in $CHCl_3$ solution at 0 °C or in the solid state at 78 °C primarily gives the dinitro complex $[Ir(Ph_2PC_2H_4PPh_2)_2(NO_2)_2]Cl$ This complex was also obtained by Vaska [17] from the reaction of $[Ir(Ph_2PC_2H_4PPh_2)_2]Cl$ and a mixture of NO and O_2 The cationic complex $[Ir(PPh_3)_2(CO)_3]BPh_4$, however, reacts with N_2O_4 to form a nitrato–nitro complex, $[Ir(PPh_3)_2(CO)(NO_2)(NO_3)_2]$ and the complex $[Ir(PPh_3)_2Cl(CO)(NO)]BF_4$ reacts with N_2O_4 to give $[Ir(PPh_3)_2(CO)(NO_2)(NO_3)Cl]$

Rhodium Complexes

The reaction of nitrogen(IV) oxide and solid *trans*-$[Rh(PPh_3)_2(CO)Cl]$ gives an intermediate Rh(III) carbonyl complex with ν(CO) at 2090 cm^{-1} compared with ν(CO) at 1960 cm^{-1} for the Rh(I) starting complex Upon warming the solid *in vacuo,* the Rh(III) product loses the CO as CO_2 to give a yellow product On the basis of the microanalytical and ir spectral data ($\nu(NO_3)$ 1555, 1535, 1380, 980, $\nu(NO_2)$ 1460, 1300, 815 cm^{-1}) we suggest that an appropriate formulation for the yellow nitro–nitrato product $[Rh_2(PPh_3)_4(NO_3)_3(NO_2)_2Cl]$ is that of a mixture of $[Rh(PPh_3)_2Cl(NO_2)(NO_3)]$ and $[Rh(PPh_3)_2(NO_3)_2(NO_2)]$ The molecular weight of the yellow product which was determined osmometrically in chloroform was found to be 778 which indicates that the compound is not a dimer (MW 1568) Repeated efforts to separate the yellow product into any components gave $[Rh(PPh_3)_2(NO_3)_2Cl]$ (*vide infra*) The formation of CO_2 and NO was observed in the reaction, but the loss of Cl presumably as NOCl was unexpected The reaction of N_2O_4 with *trans*-$[Rh(PPh_3)_2(CO)Cl]$ in cold toluene gave a green material which had ν(CO) at 2080 cm^{-1} and ν(NO) at 1640 cm^{-1} This green product could not be fully characterized since removal of solvent at room temperature *in vacuo* or upon warming in toluene at 80 °C led to disappearance of ν(CO) and ν(NO) and formation of the yellow nitrato–nitro product $[Rh_2(PPh_3)_4(NO_3)_3(NO_2)_2Cl]$ In an attempt to elucidate the nature of the yellow nitrato–nitro product which appears to have an unexpected stoichiometry, several reactions were investigated Treatment of the compound in CH_2Cl_2 with CO gave *trans*-$[Rh(PPh_3)_2(CO)Cl]$ Hydrogen chloride briefly bubbled into a yellow solution of the compound in CH_2Cl_2 gave an immediate color change to red, the compound $[Rh(PPh_3)_2Cl_2(NO_3)]$ was then isolated from the solution This experiment supports formulation of the yellow product as a nitro–nitrato complex instead of a complex containing bridging or terminal NO which would be expected to give $[Rh(PPh_3)_2Cl_2NO]$ An excess of hydrogen chloride reacting over a 12 hr period gave a product with complete substitution of the nitro and nitrato ligands

The formation of a green intermediate in the reaction of N_2O_4 with $[Rh(PPh_3)_2(CO)Cl]$ is reminiscent of the formation of green five coordinate d^6 complexes, for example in the reaction of sulfonyl halides with $[Ir(PPh_3)_2Cl(N_2)]$ [20] The reaction of $NOBF_4$ with $[Rh(PPh_3)_2(CO)Cl]$ was thus studied and found to give a green solution which had ν(CO) at 2090 cm^{-1} and ν(NO) at 1775 and 1730 cm^{-1} which would be expected for $[Rh(PPh_3)_2Cl(CO)(NO)]BF_4$ The iridium analog of this compound is, of course, the first example of a metal-nitrosyl complex with a bent M–N–O bond [15] Addition of LiCl to the solution of $[Rh(PPh_3)_2(CO)Cl(NO)]BF_4$ gave the compound $[Rh(PPh_3)_2Cl_2NO]$ in high yield

The reaction of *trans*-$[Rh(PPh_3)_2(CO)Cl]$ and N_2O_4 in dichloromethane gives the yellow nitro–nitrato product described above and an orange–red product $[Rh(PPh_3)_2Cl_2(NO_3)]\cdot 4/3CH_2Cl_2$ This compound which has ir frequencies which are attributed to nitrato vibrations (Table I) may also be prepared from the reactions of $[Rh(PPh_3)_2Cl_2(NO)]$ and NO or NO_2, or the photoreaction of O_2 with $[Rh(PPh_3)_2Cl_2(NO)]$ Carbon monoxide reacts with $[Rh(PPh_3)Cl_2(NO_3)]$ to give mainly $[Rh(PPh_3)_2Cl_2(NO)]$ and $[Rh(PPh_3)_2(CO)Cl]$ The orange–red compound $[Rh(PPh_3)_2Cl_2(NO_3)]$ is similar to the monomeric complexes $[L_2RhCl_2(NO_3)]$ (L = Ph_2MeP or Ph_2MeAs) which were prepared from the reactions of nitric acid and α- and β-$[L_3RhHCl_2]$ and $[L_3RhCl_3]$ [24] The nmr spectra for $[L_2RhCl_2(NO_3)]$ indicate equivalent ligand L groups, but whether the nitrato ligand is mono- or bi-dentate is still not known [24] The reactions of N_2O_4 with the rhodium complexes are summarized in Scheme I

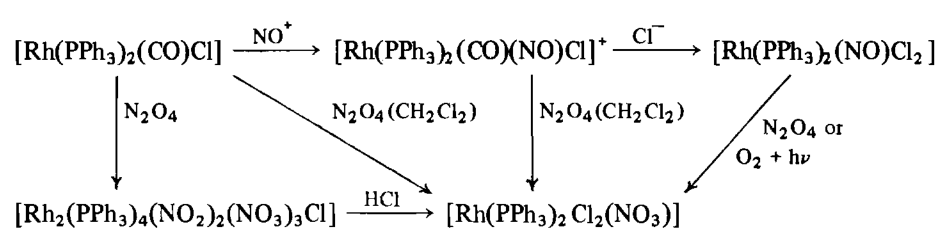
A comparison of the reactions of NO and NO_2 with complexes of the d^8 and d^{10} metals may be of value Whereas $[Pt(PPh_3)_3]$ reacts with NO to form the hyponitrite species $[Pt(PPh_3)_2(N_2O_2)]$ [4a], the reaction of $[Pt(PPh_3)_2C_2H_4]$ with NO_2 gives $[Pt(PPh_3)_2(NO)(NO_3)]$ The reactions of NO with d^8 complexes are generally given by

$$M + 4\,NO \rightarrow M(NO_2)(NO) + N_2O \qquad (3)$$

whereas with NO_2, the general course of reaction is

$$M + 3NO_2 \rightarrow M(NO_3)(NO_2) + NO \qquad (4)$$

Thus it is seen that the d^8 metal complexes provide a pathway for disproportionation of NO into N_2O



Scheme I

and NO_2^-, and NO_2 into NO and NO_3^-. From the observations made in this study, a plausible scheme for reactions of nitrogen(IV) oxide might include the following steps:

$$\text{(a)}\quad M + N_2O_4 \longrightarrow [M{-}NO]^+ + NO_3^-$$

$$\text{(b)}\quad [MNO]^+ + NO_3^- \longrightarrow [M(NO)(ONO_2)]$$

$$\text{(c)}\quad [M(NO)(ONO_2)] + NO_2 \longrightarrow [M(NO_2)(ONO_2)] + NO$$

At low temperature or during the initial stages of reaction when transitory intermediates may be observed, the reactions of N_2O_4 appear to parallel the reactions of NO^+. For example, the reaction of N_2O_4 with *trans*-$[Rh(PPh_3)_2(CO)Cl]$ gave a detectable green nitrosyl product which resembles the green product obtained from the reaction of $NOBF_4$. The observation that the reactions of N_2O_4 with $[Ir(PPh_3)_2(CO)Cl(NO)]^+$ and $[Rh(PPh_3)_2Cl_2(NO)]$ (compounds which can be readily prepared from $NOBF_4$) give the same products as those obtained from the reactions of nitrogen(IV) oxide with the parent metal carbonyls, provides strong support for the involvement of step (a). Whether this reaction proceeds by a 2-electron nucleophilic attack on the NO^+ entity in N_2O_4 or a radical (NO•) addition step cannot be readily established from these studies. However, it is interesting to note that the relatively poor donor complex $[Ir(Ph_2PCH_2CH_2PPh_2)_2]^+$ gives a dinitro species which very likely results from the addition of two •NO_2 radicals. The radical addition mechanism appears to be observed primarily in oxidative addition processes involving poor oxidants or reductants [3]. Atom transfer processes, for example the transfer of oxygen from nitrato to CO, were more predominant in the more labile rhodium complexes than in the iridium complexes.

Acknowledgements

We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work, and the Research Corporation for a Cottrell College Science Grant. Assistance from the Lilly Endowment Program is also gratefully acknowledged.

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