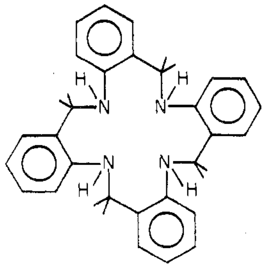

X

parent ion at *m/e* 420, which is the mass number for $C_{28}H_{22}N_4^+$ or H_8TAAB^+ cation. No nonintegral mass number absorptions (which arise when a species is doubly charged and has an odd mass number) are observed in the mass spectrum of H_8TAAB. This is in contrast to the behavior of the diacid salts and the isomers of H_4TAAB, where numerous nonintegral absorptions are seen, beginning with the *m/e* 206 (B/2) isotope envelope. The phenomenon can be rationalized if it is assumed that π electrons of imine bonds are most susceptible to scattering. Electron loss from two (or more) such bonds (leading to heteroatom cation stabilization) would lead to multicharged species.

A nickel complex of the H_8TAAB ligand was prepared and the infrared spectrum of the product contains no $\nu_{C=N}$ absorption and is congruent with that of a sample of NiH_8TAAB^{2+} prepared by other means.[19]

Acknowledgment. These studies were supported by Grant No. GM 10040 from the National Institute of General Medical Sciences of the U.S. Public Health Service.

Registry No. $TAAB(HBF_4)_2$, 62609-18-1; $TAAB(HBr)_2$, 62637-56-3; $TAAB(HClO_4)_2$, 62609-19-2; $TAAB(CF_3SO_3H)_2$, 62609-20-5; $TAAB(H_2SO_4)_2$, 62609-21-6; $TAAB(HCl)_2$, 62609-22-7; trimer (II), 25334-63-8; *o*-aminobenzaldehyde, 529-23-7; HBF_4, 16872-11-0; HBr, 10035-10-6; $HClO_4$, 7601-90-3; HCF_3SO_3, 1493-13-6; H_2SO_4, 7664-93-9; HCl, 7647-01-0; $NiTAAB(BF_4)_2$, 14286-44-3; $[Fe(TAAB)(CH_3CN)_2](BF_4)_2$, 62637-62-1; $[Fe(TAAB)(C_5H_5N)_2](BF_4)_2$, 62637-64-3; $[Rh(TAAB)(CH_3CN)_2](ClO_4)_3$, 62637-66-5; H_4TAAB (yellow isomer), 62609-23-8; H_4TAAB (white isomer), 62609-24-9; H_8TAAB, 62609-25-0.

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Quinone Adducts of Transition Metal Nitrosyl Complexes

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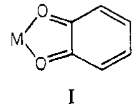
The results of the interaction of complexes of the type $M(NO)(CH_3CN)_2L_2^{2+}$ (M = Rh, Ir; L = $P(C_6H_5)_3$, $As(C_6H_5)_3$) with *o*-quinones and *o*-catechols in alcohol or diethyl ether are reported. The compounds obtained are pentacoordinate and tetracoordinate nitrosyl catecholato complexes, which differ for the nitrosyl bonding mode and the metal oxidation state. The tetracoordinate complex achieves pentacoordination by reversible addition of triphenylphosphine. The individual reaction steps have been studied in order to elucidate the metal complex and *o*-quinone chemical behavior. An alkoxide intermediate complex has been isolated in the iridium case and its chemistry studied. A parallel study with iridium arsine complexes has been done to establish the neutral ligand influence on the reaction. The simultaneous presence of the two ligands nitrosyl and quinone, for which different coordination modes are possible, confers upon the complexes a particular flexibility.

Introduction

Transition metal complexes of *o*-benzoquinones have been known for many years, but only recently have significant steps been taken to understand the nature of the metal–quinone bond. Three different coordination modes are possible for *o*-benzoquinones, differing in the formal oxidation state of the ligand



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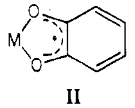

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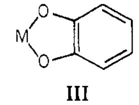


III

The relative importance of the configurations I and III should depend on the basicity of the metal and on the oxidizing ability of the quinone itself. Among the earliest reports of *o*-benzoquinone coordination are examples of complexes with metals of low basicity.[1] The weaker oxidants 9,10-phenanthrenequinone and 1,2-naphthoquinone react with difficulty and often form complexes with metals (i.e., Zn(II), Mo(IV)) for which the olefin coordination is unlikely; these complexes probably contain unreduced quinone ligands.[2] Addition reactions of *o*-benzoquinones with a variety of nucleophilic group 8 metal complexes with d^8 and d^{10} electronic metal configuration have been studied.[3-10] On coordination the qui-

Table I. Physical Data of Nitrosyl Complexes

No.	Complex	ν(NO),[a] cm^{-1}	Other freq,[a] cm^{-1}	NMR data	Λ_M,[b] Ω^{-1} cm^2 mol^{-1}
1a	$Ir(NO)(CH_3CN)_2(P(C_6H_5)_3)_2^{2+}$	1540 vs	2285 w (C≡N)	τ(H) 7.80 (6, methyl)[c] ^{31}P 13.27 ppm ($P(C_6H_5)_3$)[c]	178.0
1b	$Ir(NO)(CH_3CN)_2(As(C_6H_5)_3)_2^{2+}$	1536 s	2280 w (C≡N)	τ(H) 7.50 (6, methyl)	179.6
2	$Rh(NO)(CH_3CN)_2(P(C_6H_5)_3)_2^{2+}$	1730 vs	2310 w (C≡N)	τ(H) 7.90 (6, methyl)[c] ^{31}P −22.39 ppm ($P(C_6H_5)_3$)[c] $^1J_{Rh-P}$ = 97 Hz[c]	187.5
3a	$Ir(NO)(1,2\text{-}O_2C_6Cl_4)(P(C_6H_5)_3)_2$	1590 s	1420 s (C–O)		
3b	$Ir(NO)(1,2\text{-}O_2C_6Br_4)(P(C_6H_5)_3)_2$	1588 s	1410 s (C–O)		
4a	$Rh(NO)(1,2\text{-}O_2C_6Cl_4)(P(C_6H_5)_3)_2$	1632 s	1422 s (C–O)		
4b	$Rh(NO)(1,2\text{-}O_2C_6Br_4)(P(C_6H_5)_3)_2$	1655 s	1412 s (C–O)		
5a	$Ir(NO)(OCH_3)(P(C_6H_5)_3)_2^+$	1840 vs		τ(H) 7.93 (3, methyl)	104.4
5b	$Ir(NO)(OCH_3)(As(C_6H_5)_3)_2^+$	1847 vs		τ(H) 7.83 (3, methyl)	98.4
6a	$Ir(NO)(OC_2H_5)(P(C_6H_5)_3)_2^+$	1862 vs		τ(H) 8.94 (3, methyl) τ(H) 6.50 (2, methylene)	95.6
6b	$Ir(NO)(OC_2H_5)(As(C_6H_5)_3)_2^+$	1850 vs		τ(H) 8.83 (3, methyl) τ(H) 6.45 (2, methylene)	97.1
7a	$Ir(NO)(n\text{-}OC_3H_7)(P(C_6H_5)_3)_2^+$	1868 vs		τ(H) 9.14 (3, methyl) τ(H) 8.84 (2, methylene) τ(H) 6.51 (2, methylene)	108.0
7b	$Ir(NO)(n\text{-}OC_3H_7)(As(C_6H_5)_3)_2^+$	1850 vs		τ(H) 9.10 (3, methyl) τ(H) 8.64 (2, methylene) τ(H) 6.47 (2, methylene)	87.8
9a	$Ir(NO)(1,2\text{-}O_2C_6Cl_4)(P(C_6H_5)_3)$	1860 vs	1421 s (C–O)		
9b	$Ir(NO)(1,2\text{-}O_2C_6Br_4)(P(C_6H_5)_3)$	1858 vs	1412 s (C–O)		
9c	$Ir(NO)(1,2\text{-}O_2C_6Cl_4)(As(C_6H_5)_3)\cdot C_6H_6$	1830 vs	1418 s (C–O)		
9d	$Ir(NO)(1,2\text{-}O_2C_6Br_4)(As(C_6H_5)_3)$	1859 vs	1410 s (C–O)		
10	$Ir(NO)(P(C_6H_5)_3)_3$	1600 s			
11	$Ir(NO)(As(C_6H_5)_3)_3$	1620 s			
12	$P(C_6H_5)_3\cdot 1,2\text{-}O_2C_6Cl_4$		1460 (C–O)		
13	$P(C_6H_5)_3\cdot 1,2\text{-}O_2C_6Br_4$		1448 (C–O)		

[a] KBr pellets. [b] In CH_3NO_2 at 25 °C. [c] Data from ref 14.

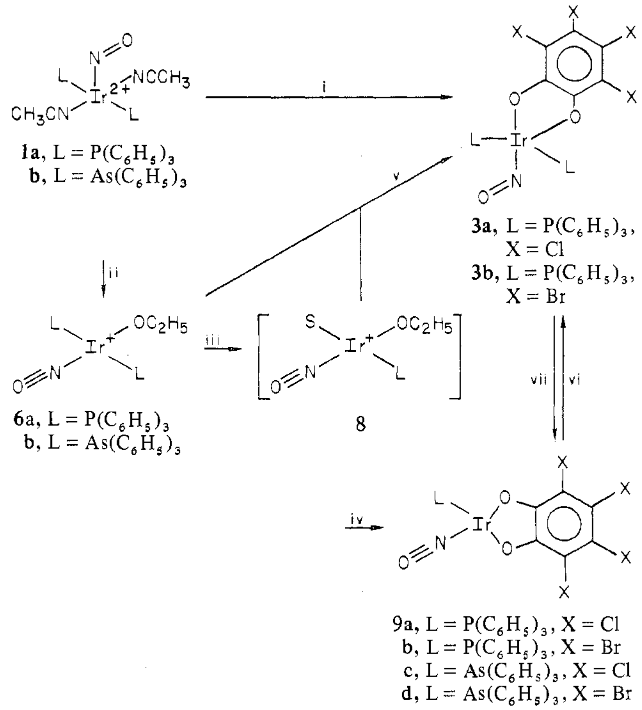
none–carbonyl stretch shifts at least 200–300 wavenumbers; this fact is diagnostic of a formal reduction to catechol with oxidation of the metal. The possibility of an intermediate radical anion coordination mode for *o*-benzoquinones has been demonstrated by the reversible chemical and electrochemical oxidation of reduced quinone complexes. Electron spin resonance spectra of these compounds (i.e., $Ir(P(C_6H_5)_3)_2COCl(O_2C_6Cl_4)^+$) indicate that the unpaired electron is localizated in the semiquinone ligand.[11] From the above it appears evident that the kinetics of the reactions and the quinone coordination mode are strongly affected by the oxidizing ability of the quinone and by the nature of the complex itself. As a part of our investigations into the chemistry of transition metal nitrosyl complexes we have studied the interaction of transition metal nitrosyl complexes with small molecules,[12,13] activated olefins,[10] and bidentate ligands[14] and their catalytic properties[15] in order to understand the role played by the nitrosyl ligand on the complex reactivity.[16]

In this paper we report the results of our investigation of the interaction between the dicationic nitrosyl complexes of the type $M(NO)(CH_3CN)L_2^{2+}$ (**1a**, M = Ir, L = $P(C_6H_5)_3$; **1b**, M = Ir, L = $As(C_6H_5)_3$; **2**, M = Rh, L = $P(C_6H_5)_3$) and *o*-benzoquinones and *o*-catechols. The compounds obtained and their selected infrared stretching frequencies and conductivity and NMR data are reported in Table I. Scheme I shows the reaction flow diagram for the iridium complex.

In this study the simultaneous presence of the nitrosyl group and of the quinone ligand is a point of particular interest. This interest arises from the ambivalent nature of the nitrosyl ligand and the possible reversible deformations from linearity of the M–N–O angles[16] which could give a greater flexibility to the real electronic density and consequently to the π–σ donor–acceptor properties of the metals in these complexes and determine the mode of the quinone coordination and vice versa.

Experimental Section

Scheme I. Flow Diagram Illustrating Iridium Nitrosyl-Catechol Complex Formation[a]



[a] Ethoxide **6** is shown; PF_6^- is not shown. i = $(C_2H_5)_2O$, 1,2-$C_6X_4(OH)_2$; ii = C_2H_5OH; iii = C_2H_5OH; iv = C_2H_5OH, 1,2-$C_6X_4O_2$; v = C_2H_5OH, 1,2-$C_6X_4(OH)_2$; vi = $(C_2H_5)_2O$, $P(C_6H_5)_3$; vii = C_2H_5OH, 1,2-$C_6X_4O_2$.

Apparatus. All of the reactions were performed in an atmosphere of nitrogen which had been purified by passing it down a column of R3-11 BASF deoxygenating catalyst and then dried over molecular sieves. The subsequent workup of the reaction mixtures was carried out in the air. Infrared spectra were recorded with a Perkin-Elmer 180 (4000–180 cm^{-1}) instrument. The solid samples were run as KBr or CsI pellets. Proton NMR spectra were obtained using a Varian Associates XL-100 12-in. spectrometer with tetramethylsilane as internal standard. NMR samples were prepared by deoxygenating the solids and the solvents with argon separately and using the needle technique for mixing. Conductivity measurements were carried out with a Jones 0.1-cm cell and a LKB 5300B Conductolyzer conductivity bridge.

The elemental analyses were determined by the Microanalysis Laboratory of the Istituto di Farmacia dell'Università di Pisa, Pisa, Italy.

Solvents and Chemicals. All the solvents were deoxygenated prior to use and the transfers were carried out with the flexible needle or syringe technique. Acetonitrile was purified as described in literature;[17] absolute ethanol was dried over 3-Å molecular sieves; reagent grade diethyl ether and hexane were purified by distillation over Na.

3,4,5,6-Tetrabromo-1,2-benzoquinone and 3,4,5,6-tetrabromo-1,2-catechol were Aldrich reagent grade products; 3,4,5,6-tetrachloro-1,2-benzoquinone was Fluka A.G. purum grade product and was used throughout. 9,10-Phenanthrenequinone and 1,2-naphthoquinone were Fluka A.G. technical grade products and were recrystallized before to use.

3,4,5,6-Tetrachloro-1,2-catechol has been prepared by reduction of 3,4,5,6-tetrachloro-1,2-quinone with triphenylphosphine in refluxing 95% ethanol.

The complexes $M(NO)(CH_3CN)_2L_2^{2+}$ have been prepared as previously reported.[14]

Preparation of $Ir(NO)(1,2\text{-}O_2C_6X_4)(P(C_6H_5)_3)_2$ (3a, X = Cl; 3b, X = Br). (i) To a suspension of 0.2 mmol of **1a** in 10 mL of diethyl ether the stoichiometric amount of the appropriate catechol in 2 mL of diethyl ether was added. The mixture was stirred at room temperature in the dark for 48 h. The light brown precipitate was filtered and recrystallized from benzene–petroleum ether to give yellow-brown microcrystals (quantitative yields).

(ii) In a typical preparation to 0.2 mmol of **6a** suspended in 5 mL of ethanol the stoichiometric amount of the appropriate catechol in 2 mL of ethanol was added. The mixture was stirred at room temperature in the dark for 48 h. The light brown precipitate was filtered and recrystallized from benzene–petroleum ether to give yellow-brown microcrystals (quantitative yields).

(iii) To a suspension of 0.2 mmol of **9a** or **9b** in 10 mL of diethyl ether the stoichiometric amount of triphenylphosphine in 3 mL of diethyl ether was added. The mixture was stirred at room temperature for 1 h. The light brown precipitate was filtered and recrystallized from benzene–petroleum ether to give yellow-brown microcrystals (quantitative yields).

Anal. Calcd for **3a**, $C_{42}H_{30}Cl_4IrNO_3P_2$: C, 50.82; H, 3.02; N, 1.41. Found: C, 51.05; H, 2.98; N, 1.45. Calcd for **3b**, $C_{42}H_{30}Br_4IrNO_3P_2$: C, 43.10; H, 2.58; N, 1.19. Found: C, 43.80; H, 2.57; N, 1.20.

Preparation of $Rh(NO)(1,2\text{-}O_2C_6X_4)(P(C_6H_5)_3)_2$ (4a, X = Cl; 4b, X = Br). To a suspension of 0.2 mmol of **2** in 5 mL of ethanol the stoichiometric amount of the appropriate catechol in 10 mL of ethanol was added. The mixture was stirred at room temperature for 2 h. The brown precipitate was filtered, washed with diethyl ether, and dried under vacuum (70% yields). Anal. Calcd for **4a**, $C_{42}H_{30}Cl_4NO_3P_2Rh$: C, 55.85; H, 3.34; N, 1.55. Found: C, 56.00; H, 3.40; N, 1.58. Calcd for **4b**, $C_{42}H_{30}Br_4NO_3P_2Rh$: C, 46.66; H, 2.79; N, 1.29. Found: C, 46.22; H, 2.80; N, 1.31.

Preparation of $Ir(NO)(OR)L_2(PF_6)$ (5a, R = CH_3, L = $P(C_6H_5)_3$; 5b, R = CH_3, L = $As(C_6H_5)_3$; 6a, R = C_2H_5, L = $P(C_6H_5)_3$). A suspension of 0.2 mmol of **1a** or **1b** in 10 mL of the appropriate alcohol was refluxed for 15 min. After cooling of the mixture, the orange crystals of **5a**, **5b**, or **6a** were removed by filtration, washed with methanol (**5a**, **5b**) or ethanol (**6a**) and hexane, and dried under vacuum (85% yield). Anal. Calcd for **5a**, $C_{37}H_{33}F_6IrNO_2P_3$: C, 48.16; H, 3.71; N, 1.51. Found: C, 47.50; H, 3.68; N, 1.59. Calcd for **5b**, $C_{37}H_{33}As_2F_6IrNO_2P$: C, 43.97; H, 3.39; N, 1.38. Found: C, 43.61; H, 3.40; N, 1.41. Calcd for **6a**, $C_{38}H_{35}F_6IrNO_2P_3$: C, 48.73; H, 3.87; N, 1.49. Found: C, 48.61; H, 3.65; N, 1.36.

Preparation of $Ir(NO)(OR)L_2(PF_6)$ (6b, R = C_2H_5, L = $As(C_6H_5)_3$; 7a, R = *n*-C_3H_7, L = $P(C_6H_5)_3$; 7b, R = *n*-C_3H_7, L = $As(C_6H_5)_3$). To a solution of **1a** or **1b** in 8 mL of methylene chloride 2 mL of the appropriate alcohol was added, and the mixture was stirred at room temperature for 3 days. After addition of 5 mL of hexane the solvent was removed under reduced pressure until orange crystals were formed. The precipitate was removed by filtration, washed with little ethyl (**6b**) or *n*-propyl alcohol (**7a**, **7b**) and hexane, and dried under vacuum (50% yield). Anal. Calcd for **6b**, $C_{38}H_{35}As_2F_6IrNO_2P$: C, 44.54; H, 3.54; N, 1.36. Found: C, 44.60; H, 3.49; N, 1.37. Calcd for **7a**, $C_{39}H_{37}F_6IrNO_2P_3$: C, 49.23; H, 3.89; N, 1.47. Found: C, 50.10; H, 3.75; N, 1.49. Calcd for **7b**, $C_{39}H_{37}As_2F_6IrNO_2P$: C, 45.06; H, 3.56; N, 1.34. Found: C, 44.50; H, 3.47; N, 1.36.

Preparation of $Ir(NO)(1,2\text{-}O_2C_6X_4)(P(C_6H_5)_3)$ (9a, X = Cl; 9b, X = Br). (i) In a typical preparation, to 0.2 mmol of **1a** suspended in 5 mL of ethanol the stoichiometric amount of the appropriate quinone in 2 mL of ethanol was added. The mixture was refluxed for 15 min. After cooling of the mixture the brown precipitate was filtered and recrystallized from benzene–petroleum ether to give brown crystals (quantitative yields). The same compounds were obtained by interaction of the alkoxide complex **6a** with the stoichiometric amount of the appropriate quinone in ethanolic solution. In the mother liquor triphenylphosphine oxide was always detected (TLC).

(ii) To a suspension of 0.2 mmol of **3a** or **3b** in 10 mL of ethanol the stoichiometric amount of quinone in 2 mL of ethanol was added. The mixture was stirred at room temperature in the dark for 24 h. The brown precipitate was filtered and recrystallized from benzene–petroleum ether to give brown crystals (quantitative yields). In the mother liquor catechol and triphenylphosphine oxide were always detected (TLC).

Anal. Calcd for **9a**, $C_{24}H_{15}Cl_4IrNO_2P$: C, 39.45; H, 2.06; N, 1.91. Found: C, 39.40; H, 2.11; N, 1.92. Calcd for **9b**, $C_{24}H_{15}Br_4IrNO_2P$: C, 31.74; H, 1.66; N, 1.54. Found: C, 32.30; H, 1.70; N, 1.51.

Preparation of $Ir(NO)(1,2\text{-}O_2C_6X_4)(As(C_6H_5)_3)$ (9c, X = Cl; 9d, X = Br). (i) In a typical preparation, to 0.2 mmol of **1b** suspended in 5 mL of ethanol the stoichiometric amount of the appropriate quinone in 2 mL of ethanol was added. The mixture was stirred at room temperature in the dark for 20 h. The brown precipitate was filtered and recrystallized from benzene–petroleum ether to give brown crystals (quantitative yields). In the mother liquor triphenylarsine oxide was always detected (TLC).

(ii) To a suspension of 0.2 mmol of **1b** in 5 mL of ethanol or diethyl ether the stoichiometric amount of the appropriate catechol in 2 mL of ethanol or diethyl ether was added. The mixture was stirred at room temperature in the dark for 48 h. The brown precipitate was filtered and recrystallized from benzene–petroleum ether to give brown crystals (quantitative yields). Triphenylarsine was always detected in the mother liquor (TLC).

Anal. Calcd for **9c**, $C_{24}H_{15}AsCl_4IrNO_2\cdot C_6H_6$: C, 42.27; H, 2.46; N, 1.64. Found: C, 42.20; H, 2.40; N, 1.69. Calcd for **9d**, $C_{24}H_{15}AsBr_4IrNO_2$: C, 30.27; H, 1.58; N, 1.47. Found: C, 30.56; H, 1.70; N, 1.42.

When these reactions were carried out with 9,10-phenanthrenequinone or 1,2-naphthoquinone, 80% of the starting alkoxide was recovered from the reaction mixture after 24-h reaction.

Preparation of $Ir(NO)L_3$ (10, L = $P(C_6H_5)_3$; 11, L = $As(C_6H_5)_3$). To a suspension of 0.2 mmol of **1a** or **1b** in 15 mL of ethanol 1 mmol of the appropriate ligand was added. The mixture was refluxed for 30 min. After cooling of the mixture the crude orange product was filtered and recrystallized from benzene–ethanol (yield: **10**, 65%; **11**, 50%). The same complexes can be obtained in the same conditions starting from **5a** or **5b**. Anal. Calcd for **10**, $C_{54}H_{45}IrNOP_3$: C, 64.15; H, 4.58; N, 1.38. Found: C, 63.68; H, 4.50; N, 1.40. Calcd for **11**, $C_{54}H_{45}As_3IrNO$: C, 56.84; H, 3.94; N, 1.22. Found: C, 57.05; H, 3.98; N, 1.20.

Preparation of $P(C_6H_5)_3\cdot 1,2\text{-}O_2C_6X_4$ (12, X = Cl; 13, X = Br). To a solution of 1 mmol of triphenylphosphine in 15 mL of diethyl ether the stoichiometric amount of the appropriate quinone in 10 mL of diethyl ether was added. The mixture was stirred for 15 min. The white precipitate was filtered, washed with diethyl ether, and dried under vacuum. Anal. Calcd for **12**, $C_{24}H_{15}Cl_4O_2P$: C, 49.65; H, 2.95. Found: C, 49.10; H, 2.87. Calcd for **13**, $C_{24}H_{15}Br_4O_2P$: C, 42.02; H, 2.20. Found: C, 42.61; H, 2.14.

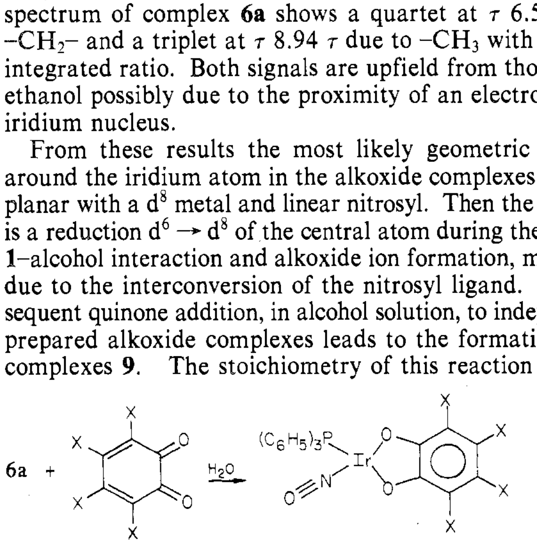
Reaction of $Rh(NO)Cl_2(P(C_6H_5)_3)_2$ with $1,2\text{-}O_2C_6Br_4$. To an ethanolic suspension of 0.2 mmol of $Rh(NO)Cl_2(P(C_6H_5)_3)_2$ the stoichiometric amount (0.2 mmol) of 3,4,5,6-tetrabromo-1,2-benzoquinone in ethanol was added. The mixture was stirred at room temperature for 24 h. The quantitative amount of the starting complex has been recovered by filtration (ν(NO) 1630 cm^{-1}).

Results and Discussion

When ethanolic suspensions of the complexes **1** react with the stoichiometric amounts of 3,4,5,6-tetrahalo-1,2-benzoquinones in ethanol, the overall products are the compounds **9** obtained in quantitative yield. The infrared spectra of these compounds, recorded as CsI pellets, show a ν(NO) stretching frequency in the 1850-cm^{-1} region (see Table I). These values for the nitrosyl stretching frequency are diagnostic of the fact that a change in the nitrosyl bonding mode is involved in the reaction **1** → **9**. Though the two limiting forms of the nitrosyl group cannot be unequivocally distinguished on the basis of ν(NO) frequency, stretching frequencies in the 1850-cm^{-1} region can be almost surely assigned to a linear nitrosyl. Upon adduct formation the quinone–carbonyl stretching vibration is lost: the presence of a band in the 1400-cm^{-1} region is consistent with the ligand reduction upon adduct formation. From the above considerations in the compounds **9** the most reasonable geometry around the metal is square planar with the metal in the d^8 configuration, the nitrosyl linearly bonded, and the quinone coordinated in its reduced diolato form (mode III). This formulation has been confirmed by elemental analysis. The most surprising result is that the reaction of strong oxidizing agents such as 3,4,5,6-tetrahalo-1,2-benzoquinones with the complex **1**, for which a d^6 metal configuration and a bent nitrosyl mode have been suggested,[14] leads to reduction of either the central atom and the quinone ligand. Quinones with a lower oxidizing power[18] such as 9,10-phenanthrenequinone or 1,2-naphthoquinone fail to react under the same reaction conditions. No isolable products are obtained if the reactions are carried out with the rhodium complex **2**. In order to explain the reaction course, the single reaction steps have been studied.

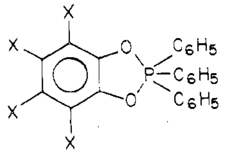
When the complexes **1** are placed in alcohol solution, the crystalline alkoxynitrosyl cation of the type $Ir(NO)(OR)L_2^+$ (**5a**, R = CH_3, L = $P(C_6H_5)_3$; **6a**, R = C_2H_5, L = $P(C_6H_5)_3$; **7a**, R = n-C_3H_7, L = $P(C_6H_5)_3$; **5b**, R = CH_3, L = $As(C_6H_5)_3$; **6b**, R = C_2H_5, L = $As(C_6H_5)_3$; **7b**, R = n-C_3H_7, L = $As(C_6H_5)_3$) can be isolated. Some of these compounds, reported in literature by Reed and Roper,[19] have been synthesized in different ways. This formulation has been confirmed by elemental analysis, proton NMR spectrum, and IR spectrum. The nitrosyl stretching frequencies are in the 1840–1870-cm^{-1} range and suggest a linear coordination mode. The ^{1}H NMR spectrum of complex **6a** shows a quartet at τ 6.50 due to $-CH_2-$ and a triplet at τ 8.94 τ due to $-CH_3$ with a correct integrated ratio. Both signals are upfield from those of free ethanol possibly due to the proximity of an electron-rich d^8 iridium nucleus.

From these results the most likely geometric situation around the iridium atom in the alkoxide complexes is square planar with a d^8 metal and linear nitrosyl. Then the net result is a reduction d^6 → d^8 of the central atom during the complex **1**–alcohol interaction and alkoxide ion formation, most likely due to the interconversion of the nitrosyl ligand. The subsequent quinone addition, in alcohol solution, to independently prepared alkoxide complexes leads to the formation of the complexes **9**. The stoichiometry of this reaction has been established. Phosphine oxide or arsine oxide is always present in the reaction mixture. As said before, the complexes **9** contain the quinone-reduced form and a linearly bonded nitrosyl group. Because phosphine oxide is the only oxidized species detectable in the reaction mixture, the 3,4,5,6-tetrahalo-1,2-benzoquinone and the phosphine must be the two species undergoing the redox process. Oxidations of tertiary phosphine with p-quinones[20] and o-quinones[21] in protic solvents have been reported in literature and postulated to occur through the formation of an intermediate quinone–phosphine adduct in which the o-quinone is trapped to form an oxyphosphorane[22] and subsequent Lewis acid catalyzed alcoholysis leads to phosphine oxide and catechol.[23] Using 3,4,5,6-tetrahalo-1,2-benzoquinones we have been able to isolate, in diethyl ether solution, the intermediate oxyphosphorane adducts **12** and **13**. These complexes in alcohol solution in presence of a metal complex can undergo alcoholysis to triphenylphosphine oxide and 3,4,5,6-tetrahalo-1,2-catechol.



9a, X = Cl
b, X = Br

$+ OP(C_6H_5)_3 + C_2H_5OH + HPF_6$



12, X = Cl
13, X = Br

The phosphine oxide or arsine oxide must be produced by the oxidation of one ligand molecule of the alkoxide complex, which must be in such a bonding situation to undergo some extent of dissociation leading to the solvate complex **8**, the actual reacting species. Consequently formation of the complexes **9** must be due to the interaction of the alkoxide species (i.e., the solvate species **8**) and the quinone-reduced form, o-catechol, the true quinoid active form in such reaction. The iridium nitrosyl moiety retains the central metal oxidation state and d^8 electronic configuration with the nitrosyl bonding mode present in the alkoxide complex situation. Following this approach o-quinones which have not the power to oxidize a phosphine molecule and produce the catecholate species in our experimental conditions, such as 9,10-phenanthrenequinone and 1,2-naphthoquinone,[24] must fail to react, as was actually found.

The reaction of the ethoxide complex **6a** in ethanol with 3,4,5,6-tetrahalo-1,2-catechols leads to the formation of the pentacoordinate nitrosyl complexes **3a** and **3b**. There is a drop of approximately 250 wavenumbers in ν(NO) during this coordination process probably corresponding to a change from a linear Ir–N–O arrangement to a bent arrangement.

The reaction of the complex **1a** in diethyl ether solution with catechols offers an alternate method of preparation for the complexes **3**. The same reaction carried out with the rhodium complex **2** leads to the formation of the complexes **4**. The IR spectra do not indicate changes in the nitrosyl mode. The pentacoordinate diolate complexes **3a** and **4a** have already been synthesized by reaction of the complexes $M(NO)(P(C_6H_5)_3)_3$, M = Ir and Rh, with excess of 3,4,5,6-tetrachloro-1,2-benzoquinone in diethyl ether–benzene solution. For these complexes a square-pyramidal geometry with the metal in the d^6 electronic state and an apical bent nitrosyl ligand has been proposed.[7] Our analytical results are consistent with a pentacoordinate situation in the case of complexes **3b** and **4b**.

The pentacoordinate triphenylphosphine complexes **3** can be obtained with a reversible coordination reaction. The tetracoordinate triphenylphosphine complexes in diethyl ether solution achieve immediately pentacoordination with triphenylphosphine to form the complexes **3**. A dramatic decrease of the ν(NO) is evidence of the change of the bonding mode during the phosphine coordination process. It is not at all surprising that a change in coordination number results in the transfer of electron density between the coordinated nitrosyl group and the metal. This type of transformation has been discussed lately by Feltham and co-workers[25] related to the interconversion of $NOCo(diars)_2^{2+}$ (Co–N–O = 178°, ν(NO)

1853 cm^{-1}) and $NOCo(diars)_2SCN^+$ (Co–N–O = 132°, ν(NO) 1537 cm^{-1}).[25b] For a pentacoordinate metal complex with a bent nitrosyl group a square-pyramidal geometry with apical nitrosyl should be expected. However, in the presence of a cis chelating ligand such as a catechol, for which the bite angle[8,27] is always less than 85°, this geometry is the less likely to occur because the two bulky phosphine ligands will be forced to occupy adjacent coordination sites. Although all of the available crystal structures for pentacoordinate trigonal-bipyramidal geometries show a nearly linear nitrosyl group, among the bent nitrosyl structures there appear to be no perfect trigonal bipyramids. Yet many of the structures identified as square pyramids are in fact intermediate in geometry between the two extremes.[28] Recently Ibers has predicted that ligands which deactivate the metal by removing electron density from it favor the trigonal-bipyramidal geometry.[26] Thus on the basis of these considerations we propose that for the nitrosyl complexes **3**, if not a trigonal-bipyramidal geometry, at least an intermediate situation between the trigonal- and square-pyramidal geometry might be considered.

The reaction (vi, see Scheme I) is just slightly reversed at room temperature. Infrared evidence supports the fact that independently prepared pentacoordinate complexes undergo a slight phosphine dissociation to form the corresponding tetracoordinate **9**. Chemical evidence of the phosphine dissociation from the pentacoordinate species **3** is the fact that if the stoichiometric amount of 3,4,5,6-tetrabromo-1,2-benzoquinone is used as phosphine scavenger in an ethanolic suspension of complex **3a**, a quantitative yield of tetracoordinate complex **9a** together with phosphine oxide and 3,4,5,6-tetrabromo-1,2-catechol is obtained. This quinone–phosphine interaction does not occur with complexes such as $Rh(NO)Cl_2(P(C_6H_5)_3)_2$ for which the absence of any phosphine dissociation has been already demonstrated.[29] When the rhodium dichloronitrosyl complex has been reacted with the stoichiometric amount of 3,4,5,6-tetrabromo-1,2-benzoquinone, the quantitative amount of unreacted compound has been recovered after 24-h reaction time. This chemical behavior of complexes **9a** and **9b** toward pentacoordination can explain why from the interaction of **6** and catechol with free phosphine solution the complexes **3** are obtained.

A parallel study has been done starting from the triphenylarsine complex **1b**. Interaction of **1b** either with quinones in alcohol or with catechols in alcohol or diethyl ether leads to the formation of complexes **9c** and **9d**. These reactions are closely related to those of the triphenylphosphine complex **1a**, but we have been unable to obtain any pentacoordinate nitrosyl arsine complex, by reaction either in diethyl ether between complex **1b** and 3,4,5,6-tetrahalo-1,2-catechol or in ethanol between the alkoxide complex **6b** and the same catecholato species. If the arsine pentacoordinate species analogous to **3** are formed, they might dissociate one arsine ligand completely. Free arsine is always present in the alcohol or diethyl ether reaction mixtures. In view of the postulated phosphine dissociation from the alkoxide complex **6a** (and of the reversibility of the triphenylphosphine addition to the complexes **9a** and **9b**), this large arsine dissociation can be due to the steric hindrance of the bulkier group 5 donor.

The reaction pathway was tested starting with several phosphine or arsine alkoxide complexes to check its actual validity. The interactions of alcohol solutions of these alkoxide complexes with the appropriate phosphine or arsine lead to the formation of the complexes **10** and **11**, of the type $Ir(NO)L_3$.

The impossibility of obtaining tetracoordinate complexes of type **9** for rhodium could be due to difficulty in forming the alkoxide complex or to its very low stability once formed.

As supposed, the simultaneous presence in the metal coordination sphere of both nitrosyl and *o*-quinone ligands confers upon the system a great flexibility and reaction reversibility. The system here reported can illustrate a potential powerful pathway for oxidation of coordinated ligands upon coordination of a species capable of undergoing the necessary redox process, while the metal–nitrosyl ligand moiety acts just as a template.

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Registry No. **1a**, 59983-15-2; **1b**, 62521-15-7; **2**, 60018-66-8; **3a**, 34511-47-2; **3b**, 62521-16-8; **4a**, 34808-09-8; **4b**, 62520-93-8; **5a**(PF_6), 62520-95-0; **5b**(PF_6), 62520-97-2; **6a**(PF_6), 62520-98-3; **6b**(PF_6), 62520-99-4; **7a**(PF_6), 62521-00-0; **7b**(PF_6), 62521-02-2; **9a**, 62521-03-3; **9b**, 62521-04-4; **9c**, 62521-05-5; **9d**, 62521-06-6; **10**, 25448-15-1; **11**, 37130-26-0; **12**, 62475-98-3; **13**, 62475-97-2.

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