CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
FACULTY OF ENGINEERING SCIENCE, OSAKA UNIVERSITY, OSAKA, JAPAN

Dioxygen Complexes of Rhodium. Halogeno(dioxygen)bis(triphenylphosphine)(isocyanide)rhodium and Related Compounds

BY AKIRA NAKAMURA,* YOSHITAKA TATSUNO, AND SEI OTSUKA

Received January 4, 1972

A variety of new dioxygen complexes of rhodium(I) of composition $RhX(O_2)(PPh_3)_2(RNC)$ (X = Cl, Br, I, R = *t*-Bu; X = Cl, R = *c*-C_6H_{11}, *p*-$CH_3C_6H_4$), $RhCl(O_2)(AsPh_3)_2(t\text{-}BuNC)$, and $[Rh(O_2)(PPh_3)_2(t\text{-}BuNC)_2]Cl$ were prepared by two methods: (a) air exposure of a solution of $RhX(PPh_3)_2(RNC)$, $RhX(PPh_3)_2(t\text{-}BuNC)_2$, or $RhCl(AsPh_3)_2(t\text{-}BuNC)$; (b) introduction of air into a reaction mixture of $RhX(PPh_3)_3$ with RNC in benzene. These novel dioxygen complexes are relatively thermally stable in the solid state. The *tert*-butyl isocyanide derivatives hold dioxygen irreversibly, whereas the analogous *p*-tolyl isocyanide analogs reversibly bind dioxygen. They are generally yellowish green to brownish yellow diamagnetic, polymeric complexes, poorly soluble in many organic solvents. The ir data of mono(*tert*-butyl isocyanide)–dioxygen complexes suggest a structure with trans halogen bridging; the same is assumed to be true for the other. A structure having two mutually trans phosphines is assumed by analogy with the analogous iridium complexes.

Introduction

The dioxygen complexes with "end-on" coordination derived from cobalt(II) ammine complexes of Schiff base chelates are well known.[1] In contrast, the non-Werner complexes of rhodium or iridium, *e.g.*, Vaska's iridium complex,[2] form dioxygen complexes with "side-on" coordination. The rhodium analog of the Vaska complex, $RhX(CO)(PPh_3)_2$, is reported to be inert to air in solution,[3] and only very recently infrared evidence for the presence of the impure dioxygen complex in solution was obtained.[4]

Formation of a dioxygen complex by aerial oxygenation of $RhCl(PPh_3)_3$ or $RhCl(AsPh_3)_3$ in CH_2Cl_2 solution has also been reported,[5] and an X-ray analysis of one of the complexes recently showed it to be binuclear with a novel dioxygen bridge.[6a] Bis(diphosphine) complexes of rhodium(I) and iridium(I) form dioxygen complexes,[6b] the process being irreversible for iridium but reversible for rhodium.[3] It would be interesting to investigate in detail the difference between rhodium and iridium in the formation of dioxygen complexes. Recently thermodynamic data were presented and compared for the reversible addition of some small molecules to isostructural d^8 complexes of rhodium and iridium.[7a] These data certainly contribute to our understanding of the interaction of small covalent molecules and transition metal atoms. However, the proposed interpretation in terms of a simple acid–base interaction[3] fails to give a consistent account for some observations, *e.g.*, an acidity order of $H_2 > O_2$ relative to the iridium complex, while for the rhodium it is the reverse, $O_2 > H_2$. Our efforts are focusing on obtaining a variety of rhodium–dioxygen complexes which are scarce in comparison with the iridium–dioxygen complexes.

In the course of our study[7b] on the catalytic oxygenation of isocyanides using nickel, palladium, cobalt, and rhodium complexes, we examined the reaction of $RhCl(PPh_3)_3$ with isocyanide and then with dioxygen. Stable dioxygen complexes of rhodium $RhX(O_2)(PR_3)_2(RNC)$ (**1**) were thus found. These new dioxygen complexes can accommodate a variety of auxiliary ligands such as halides, isocyanides, phosphines, or arsines, a feature relevant to a study of the ligand effect on dioxygen coordination. The parent rhodium(I) complexes, $RhX(PR_3)_2(RNC)$ and $[Rh(PR_3)_2(RNC)_2]X$, add various small molecules, *e.g.*, X_2, CH_3I, CS_2, CO, TCNE, etc., and seem to be promising compounds for detailed study of the bonding between the metal and the small molecules. After completion of our research the methyl isocyanide analog of the dioxygen complex $RhCl(O_2)(PPh_3)_2(CH_3NC)$ was reported[8] briefly together with some related oxidative adducts with TCNE, iodine, and mercuric chloride.

In this paper the preparation and spectroscopic investigation[9] of new dioxygen–rhodium complexes are reported.

Results and Discussion

Preparative Chemistry and Properties. (a) Parent Complexes.—The parent rhodium(I) complexes of the type $RhX(PPh_3)_2(RNC)$ (**2**) are prepared by addition of 1 mol of an isocyanide to a benzene solution or suspension of $RhX(PPh_3)_3$ under nitrogen at room temperature. The halogen-bridged complexes $[RhX(L)_2]_2$ (L = PPh_3, $AsPh_3$) may also be used. These crystalline complexes prepared from *t*-BuNC are relatively stable in air when completely dry, but they readily take up dioxygen when wet with solvents such as benzene. The ir and ^1H nmr spectra (*vide infra*) are consistent with a square-planar, diamagnetic complex. The two phosphine ligands are most probably in trans configuration as in many other Rh(I) and Ir(I) square-planar bis(phosphine) complexes (*vide infra*).

---

[1] (a) L. H. Vogt, Jr., H. M. Faigenbaum, and S. E. Wiberly, *Chem. Rev.*, **63**, 269 (1963); (b) J. A. Connor and E. A. V. Ebsworth, *Advan. Inorg. Chem. Radiochem.*, **6**, 279 (1964); (c) R. G. Wilkins, *Advan. Chem. Ser.*, **No. 100**, 111 (1970); (d) H. B. Gray, *ibid.*, 382 (1970).

[2] L. Vaska, *Science*, **140**, 809 (1963); L. Vaska and D. L. Catone, *J. Amer. Chem. Soc.*, **88**, 5324 (1966).

[3] L. Vaska, *Accounts Chem. Res.*, **1**, 335 (1968).

[4] G. T. Mortimer and S. J. Ashcroft, *Inorg. Chem.*, **10**, 1326 (1971).

[5] J. T. Mague and G. Wilkinson, *J. Chem. Soc. A*, 1736 (1966).

[6] (a) M. J. Bennett and P. B. Donaldson, *J. Amer. Chem. Soc.*, **93**, 3307 (1971); (b) J. A. McGinnety, N. C. Payne, and J. A. Ibers, *ibid.*, **91**, 6301 (1969).

[7] (a) L. Vaska and L. S. Chen, *Chem. Commun.*, 1080 (1971); (b) S. Otsuka, A. Nakamura, and Y. Tatsuno, *ibid.*, 836 (1967); *J. Amer. Chem. Soc.*, **91**, 6994 (1969).

[8] A. L. Balch and J. Miller, *J. Organometal. Chem.*, **32**, 263 (1971).

[9] An ^{18}O-isotopic infrared study of some of the complexes has already been published: A. Nakamura, Y. Tatsuno, M. Yamamoto, and S. Otsuka, *J. Amer. Chem. Soc.*, **93**, 6052 (1971).

$$\mathrm{RhX(PPh_3)_3 + RNC \longrightarrow RhX(PPh_3)_2(RNC) + PPh_3}$$

When 2 molar equiv of *t*-BuNC was added to $\mathrm{RhCl(PPh_3)_3}$ or $\mathrm{RhBr(PPh_3)_3}$ in benzene, yellow precipitates of the formula $\mathrm{RhX(PPh_3)_2(\textit{t}\text{-}BuNC)_2 \cdot C_6H_6}$ (X = Cl or Br) were formed. These complexes are 1:1 electrolytes in methanol or in dichloromethane and consistently lack the Rh–X stretching band in the infrared. When completely dry, they are stable in air, but they take up dioxygen slowly in solution. The ir spectrum showing one NC stretching absorption at 2120 $\mathrm{cm^{-1}}$ is consistent with the trans square-planar rhodium(I) cation $[\mathrm{Rh(PPh_3)_2(\textit{t}\text{-}BuNC)_2}]^+$. Interestingly, similar bis(aryl isocyanide) complexes $[\mathrm{Rh(ArNC)_2(PPh_3)_2}]\mathrm{X}$, reported by Vallarino,[10] provide TCNE adducts[11] but no dioxygen complexes.

$$\mathrm{RhX(PPh_3)_3 + 2RNC \longrightarrow [Rh(PPh_3)_2(RNC)_2]X + PPh_3}$$

(b) **Dioxygen Complexes.**—The dioxygen complexes of $\mathrm{RhXL_2(RNC)}$ (L = $\mathrm{PPh_3}$, $\mathrm{AsPh_3}$) can be prepared by two general methods: the aerial oxygenation of either the parent complexes or the orange reaction mixture formed by addition of 1 mol of an isocyanide to $\mathrm{RhXL_3}$ (L = $\mathrm{PPh_3}$, $\mathrm{AsPh_3}$) or $[\mathrm{RhXL_2}]_2$ (L = $\mathrm{AsPh_3}$). The dioxygen complexes (**1a**, **1b**) are obtained as pale green or greenish yellow poorly soluble precipitates. The precipitation is apparently due to polymerization of the solvated dioxygen complex releasing the solvent molecules. In some cases, *e.g.*, **1c** (R = *p*-tolyl), the pale brownish yellow precipitate forms only after concentration of the oxygenated solution under reduced pressure. This behavior suggests an enhanced solubility of the solvated dioxygen complex and a reduced tendency for polymerization compared with the *tert*-butyl analog **1a**. Although the unsolvated dioxygen complex **1c** shows limited solubility in noncoordinating solvents, it redissolves in polar coordinating solvents such as dichloromethane or chloroform to some extent. Analytical and spectroscopic data are given in Tables I and II.

$$\underset{\mathbf{2}}{\mathrm{RhX(L)_2(RNC)}} + \mathrm{O_2} \longrightarrow \underset{\mathbf{1}}{\mathrm{RhX(O_2)(L)_2(RNC)}}$$

Conversion into the dioxygen complex was readily followed by the shift of the ir C≡N stretching band toward higher frequency and also by the appearance of a strong band at *ca.* 890 $\mathrm{cm^{-1}}$. A weak band around 570–580 $\mathrm{cm^{-1}}$ is also characteristic of the dioxygen complex.[12] The ^{1}H nmr spectra do not serve to diagnose the dioxygen complex formation of **1a** as will be shown later. Formation of the dioxygen complex $\mathrm{RhCl(O_2)(PPh_3)_2(CH_3NC)}$ was detected by the strong ir band at 888 $\mathrm{cm^{-1}}$ without isolation. The reaction of $\mathrm{RhCl(AsPh_3)_3}$ with *t*-BuNC followed by exposure to air gave only a small amount of the expected dioxygen complex. The dioxygen complex **1g** containing triphenylarsine was obtained as a green powder by exposure to air of the orange solution formed by addition of *t*-BuNC to $[\mathrm{RhCl(AsPh_3)_2}]_2$ (2:1) in benzene. The failure to obtain the dioxygen complex directly from $\mathrm{RhCl(AsPh_3)_3}$ may imply blockage of coordination site by unoxidizable bulky triphenylarsine.

A pale brown dioxygen complex **1h** was obtained by oxygenation of a $\mathrm{CH_2Cl_2}$ solution of the bis(isocyanide) complex, $[\mathrm{Rh(PPh_3)_2(\textit{t}\text{-}BuNC)_2}]\mathrm{Cl}$. It is soluble in polar organic solvents suggesting its electrolytic property. When the oxygenation was carried out in toluene suspension a different dioxygen complex formed as a precipitate which could not be purified.

Addition of more than 3 equiv of *t*-BuNC to $\mathrm{RhCl(PPh_3)_3}$ followed by aerial oxygenation failed to give any dioxygen complex. The tetrakis(isocyanide)rhodium(I) cation was also inactive toward dioxygen. Similarly, the trisphosphine complex of Co(I) or Ir(I), *e.g.*, $\mathrm{CoCl(PPh_3)_3}$ or $\mathrm{IrCl(PPh_3)_3}$, did not give the corresponding isocyanide–dioxygen complex upon addition of RNC and air.

Once formed as precipitates the monoisocyanide–dioxygen complexes **1a**, **b** are practically insoluble in many organic solvents such as THF, $\mathrm{CHCl_3}$, pyridine, etc. The orange dilute solution of the dioxygen complex (**1a**) in boiling $\mathrm{CH_2Cl_2}$ decomposes slowly yielding $\mathrm{Ph_3PO}$ and unidentified brown semisolid. The dissolution with partial decomposition is also observed for solvents such as $\mathrm{CH_2Br_2}$, $\mathrm{CHCl_3}$, and PhCl at their boiling points. The molecular weight of **1a** in $\mathrm{CHCl_3}$ at 20° indicates its monomeric nature, but there is partial decomposition. The stability of the dioxygen complex is therefore clearly due to some stabilizing intermolecular interaction forming a coordination polymer in the solid state. These dioxygen complexes of rhodium can be regarded as isocyanide analogs of Vaska's dioxygen complex $\mathrm{IrCl(O_2)(PPh_3)_2(CO)}$, but the rhodium analog of Vaska's complex, $\mathrm{RhCl(CO)(PPh_3)_2}$, fails to give the corresponding dioxygen derivatives.[3] The apparent thermal stability as inferred from the decomposition points and the yield depends on the isocyanide ligand and decreases on going from *t*-butyl to cyclohexyl to *p*-tolyl isocyanide. Variation of halogen ligand of **1a** did not show any remarkable effect on the thermal stability. The triphenylarsine analog is found to be thermally more stable than the triphenylphosphine complex as the decomposition points indicate.

The bis(isocyanide)–dioxygen complex **1h** is apparently more soluble in organic solvents, and the solution was stable for at least a few hours at room temperature.

(c) **Reversibility of Dioxygen Coordination.**—**1a** or **1b** in benzene suspension was stirred under reflux in $\mathrm{N_2}$ for 2 hr, resulting in decomposition to a brown solution. Among the products, triphenylphosphine oxide was identified. **1a** or **1b** remained unchanged on evacuation to 1 mm at 22–90° for 2 hr. On irradiation with sunlight under $\mathrm{N_2}$, however, decomposition to brown solids occurred.

In contrast to the behavior of these derivatives, the analogous complex of *p*-tolyl isocyanide (**1c**) shows reversibility upon dioxygenation. Thus a chloroform solution of **1c** readily reverts to the starting material **2b** on stirring in nitrogen atmosphere at 0° for *ca.* 1 hr. The bis(isocyanide)–dioxygen complex **1h** does not dissociate dioxygen upon evaporation of the solution to dryness.

(d) **Reactions.**—The reactivity of the monoisocyanide–dioxygen complex is briefly surveyed as well as its catalytic activity. Reaction with iodine occurred readily at room temperature in $\mathrm{CH_2Cl_2}$ with evolution

---

(10) L. Vallarino, *Gazz. Chim. Ital.*, **89**, 1632 (1959).

(11) T. Boschi, P. Uguagliati, and B. Crociani, *J. Organometal. Chem.*, **30**, 283 (1971).

(12) These two ir bands are assigned to mutually mixed vibrations of $\nu_{\mathrm{O-O}}$ and $\nu_{\mathrm{M-O}}$, respectively.[9]

TABLE I

PHYSICAL PROPERTIES AND ANALYTICAL DATA[a]

				Elemental analysis, %				
No.	Compound	Appearance	Mp, °C	C	H	N	O	Halogen
1a	RhCl(O$_2$)(PPh$_3$)$_2$(*t*-BuNC)[b]	Green powder	147–150 dec	63.14 (63.19)	5.29 (5.05)	1.76 (1.80)	4.39 (4.11)	4.7 (4.5)
1b	RhCl(O$_2$)(PPh$_3$)$_2$(C$_6$H$_{11}$NC)	Greenish yellow powder	130 dec	64.08 (64.22)	5.18 (5.10)	1.69 (1.74)	3.39 (3.98)	
1c	RhCl(O$_2$)(PPh$_3$)$_2$(*p*-CH$_3$C$_6$H$_4$NC)	Pale yellowish brown powder	117–118 dec	65.41 (65.20)	4.95 (4.61)	1.61 (1.72)	3.13 (3.94)	4.30 (4.38)
1d	RhBr(O$_2$)(PPh$_3$)$_2$(*t*-BuNC)	Greenish yellow powder	150 dec	61.07 (59.98)	4.78 (4.73)	1.69 (1.70)		9.64 (9.73)
1e	RhBr(O$_2$)(PPh$_3$)$_2$(C$_6$H$_{11}$NC)	Greenish yellow powder	120–121 dec	60.10 (60.86)	4.98 (4.88)	1.52 (1.65)	4.38 (3.77)	7.21 (9.42)
1f	RhI(O$_2$)(PPh$_3$)$_2$(*t*-BuNC)	Yellow powder	153–155 dec	57.62 (56.62)	4.58 (4.49)	1.56 (1.61)		
1g	RhCl(O$_2$)(AsPh$_3$)$_2$(*t*-BuNC)	Green cryst	180 dec	58.43 (56.87)	4.83 (4.56)	1.60 (1.62)		3.98 (4.12)
1h	[Rh(O$_2$)(PPh$_3$)$_2$(*t*-BuNC)$_2$]Cl·$^1/_2$CH$_2$Cl$_2$	Pale brown microcrystals	139 dec	61.33 (61.80)	5.67 (5.46)	3.14 (3.10)		
2a	RhCl(PPh$_3$)$_2$(*t*-BuNC)	Orange plates	240–245 in N$_2$ 155–160 dec in air	66.08 (66.01)	5.48 (5.27)	1.89 (1.88)		5.04 (4.77)
2b	RhCl(PPh$_3$)$_2$(*p*-CH$_3$C$_6$H$_4$NC)	Orange cryst	180–195 dec in air	67.80 (67.88)	4.78 (5.15)	1.82 (1.795)		5.48 (4.55)
2c	RhBr(PPh$_3$)$_2$(*t*-BuNC)	Orange plates	225–230 in N$_2$ 166–168 in air	64.81 (65.00)	5.27 (5.23)	1.84 (1.61)		10.78 (9.20)
2d	RhI(PPh$_3$)$_2$(*t*-BuNC)	Orange cryst	148–149 in air	59.41 (58.80)	5.24 (4.70)			
3a	RhCl(PPh$_3$)$_2$(*t*-BuNC)$_2$·C$_6$H$_5$	Yellow powder	175–176 in N$_2$ 143–146 in air	68.29 (68.84)	6.02 (6.00)	2.86 (3.09)		
3b	RhBr(PPh$_3$)$_2$(*t*-BuNC)$_2$·C$_6$H$_6$	Yellow powder	168–170 in air	65.40 (65.62)	5.60 (5.72)	2.62 (2.94)		9.1 (8.4)
4	RhCl(PPh$_3$)$_2$(*t*-BuNC)TCNE·CH$_2$Cl$_2$	Lemon yellow	210–215 in air	60.59 (60.11)	4.33 (4.31)	7.41 (7.30)		
5	RhBr(SO$_2$)(SO$_4$)(PPh$_3$)$_2$(*t*-BuNC)	Orange powder	220 dec	51.75 (51.80)	4.58 (4.13)	1.41 (1.47)		

[a] Calculated values in parentheses. [b] Analysis of phosphorus was performed only for this complex: found, 7.80%; calcd, 7.96%. A sample prepared in CH$_2$Cl$_2$ and containing 1 mol of CH$_2$Cl$_2$ showed a halogen content of 9.56% (calcd 8.65%).

TABLE II

INFRARED[a,b] AND ELECTRONIC SPECTRA

	1a	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**	**1h**	**2a**	**2b**
$\nu_{C\equiv N}$	2149	2170	2145	2152	2165	2151	2145	2203 2183	2095	2125
ν_{Rh-Cl}	291	293	300				295		312	310
ν_{O-O}[c]	892	893	889	892	892	893	884	891		
ν_{Rh-O}[c]	576	579	590	572	581	565	579			
λ_{max}[d] (log ϵ)	310 (4.24)		313 sh (4.27)	313 sh (4.11)	320 sh (4.25)	410 sh (3.0)			373 (3.64)	390 sh (3.6)
In soln	285 (4.23)		280 (4.38)	290 (4.23)	290 (4.39)	295 (4.32)			304 (4.19)	314 (4.21)
λ_{max}[e] (solid state)	629	640		670	680	650 sh	605			

[a] For the infrared data of complexes **2c**, **2d**, **3a**, **3b**, **4**, **5**, see Experimental Section. [b] Only the important absorptions are listed in cm^{-1}. [c] This is neither the "pure" O–O nor Rh–O stretching mode (*cf.* ref 9). [d] In dichloromethane solution. λ_{max} in nm. [e] Reflectance. Shimadzu Model MPS-50L with a reflectance attachment, no reference sample, no dilution. The sample taken in between thin glass plates (ordinary glass) which have no absorption in the 350–800-nm range.

of O$_2$. The similar reaction with liquid bromine proceeds vigorously. Heating of the parent complex with TCNE in benzene gives a TCNE complex, RhCl(TCNE)(PPh$_3$)$_2$(*t*-BuNC). In contrast, a similar reaction of a dioxygen complex **1a** with TCNE gives a deep green amorphous solid which resists all attempts at purification. In liquid sulfur dioxide at −20°, the dioxygen complex **1a** turns into a yellow solid soluble in liquid SO$_2$. Elemental analysis indicates a composition RhBr(SO$_4$)(SO$_2$)(PPh$_3$)$_2$(*t*-BuNC). These reactions are very similar to those observed in the isocyanide–dioxygen complex of nickel and palladium.[7b] Catalytic oxygenation of PPh$_3$ occurs in toluene at 110° under 1 atm of O$_2$ to produce OPPh$_3$. Similarly catalytic oxygenation of *t*-BuNC proceeds at 80° in benzene to give *t*-BuNCO. The catalytic activity of the rhodium complex is lower compared with that of nickel or palladium isocyanide–dioxygen complexes.[7b]

The halogen exchange reaction of the chloro– or bromo–dioxygen complexes readily occurs by mixing the CH$_2$Cl$_2$ suspension with an excess of tetra-*n*-butylammonium iodide at room temperature. Thus the iodo–dioxygen complex is obtainable from the corresponding chloro or bromo derivative. The extent of the halogen exchange is conveniently and easily followed by the change in electronic spectra in CH$_2$Cl$_2$ solution. This technique revealed that the direction of the exchange greatly favors the iodo derivative.

The rate of thermal decomposition in dilute CH$_2$Cl$_2$ solution can be followed by the change in electronic spectra. A relative order of the solution stability decreases on going from the *tert*-butyl isocyanide to the *p*-tolyl isocyanide derivative (**1a** > **1b** > **1c**).

Spectra and Structure. (a) **Nmr Spectra.**—The nmr data of the monoisocyanide–dioxygen complexes are difficult to obtain because of the insolubility of the complexes in usual nmr solvents. **1a**, **1d**, and **1f** are only slightly soluble in boiling CH_2Cl_2 with partial decomposition. We have taken advantage of the *in situ* formation of the dioxygen complex from the CH_2Cl_2 solution of **2a**. Thus, the nmr spectrum of **2a** in cold CH_2Cl_2 was first measured under nitrogen, and then the solution was exposed to air. That the dioxygen complex forms immediately in CH_2Cl_2 solution on exposure to air was confirmed using ir spectroscopy. No precipitates of dioxygen complex formed by this technique even in a concentration sufficient to observe an nmr spectrum. The nmr data of this dioxygenated solution were almost identical with those of the unoxygenated solution which showed peaks at τ 9.53 (9 H, singlet) and 2.20, 2.55 (30 H, broad multiplets). These results indicate that the chemical shift of the *tert*-butyl and phenyl protons of **2a** are not sensitive to the addition of dioxygen on the central metal. Therefore, no great structural change on dioxygenation is suggested.

The nmr spectrum of **2b** in $CDCl_3$ showed peaks at τ 2.25, 2.68 (multiplet, 30 H, Ph_3P protons), 3.38 (doublet, J = 7 Hz, 2 H), 4.31 (doublet, J = 7 Hz, 2 H), and 7.89 (singlet, 3 H, CH_3). The pairs of doublet peaks at τ 3.38 and 4.31 are identified as the ring protons of the *p*-tolyl group. They are shifted upfield in comparison with the free ligand (at τ 2.7). This diamagnetic shift may well be due to the increased electron density on the aromatic ring by the back-bonding effect. The enhanced back-bonding in the case of *p*-tolyl isocyanide implies a reduced electron density on the rhodium in comparison with the *tert*-butyl analog. This is clearly manifested in the reversibility of the dioxygen coordination in **1c** as described above. Change of the ^1H nmr spectrum of **2b** was observed by introduction of dioxygen into the $CDCl_3$ solution during the measurement. New signals due to the formation of dioxygen complex appeared at τ 2.30, 2.68 (multiplet 30 H, Ph_3P protons), 3.12 (doublet J = 7 Hz, 2 H), 3.98 (doublet, J = 7 Hz, 2 H), and 7.77 (singlet, 3 H, CH_3). The observed paramagnetic shifts relative to the reasonance of the parent compound, *i.e.*, τ 3.38–3.12 and τ 4.31–3.98 (aromatic protons), are explicable in terms of reduced electron density on the rhodium by the dioxygen addition.

(b) **Infrared Spectra.**—Detailed ^{18}O isotopic ir study has been made. Some of the important results are briefly cited here (*cf.* Table II). (1) An increase in ν_{CN} on O_2 addition occurs in general. (2) The complexed O_2 stretching (ν_{O-O}) is remarkably constant, and the trend on variation of auxiliary ligands is irregular; a significant mixing of O–O and M–O_2 stretching vibrations appears to be responsible for this irregularity. (3) Some increase in ν_{RhCl} is observed with decreasing electron donor ability of the isocyanides. (4) A calculation of approximate force constants for the Rh–O bond indicates a relatively strong rhodium–oxygen bond ($f_{RhO} = \sim 3.2$ mdyn/Å)[9] compared to Pt(0)–O_2 (2.1 or 2.2 mdyn/Å),[9] and the force constant for O–O bond (*ca.* 3.3 mdyn/Å)[9] is of a similar order to that found in excited triplet dioxygen ($^3\Sigma_u^+$ or $^3\Sigma_u^-$).

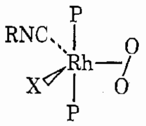
The ν_{CN} data of various complexes prepared by oxidative addition on $RhCl(PPh_3)_2(t\text{-}BuNC)$ can be used to compare the electron density on the rhodium atom. Thus, the ν_{CN} of the O_2 complex (2150 cm^{-1}) is lower than that of the TCNE complex, $RhCl(PPh_3)_2(t\text{-}BuNC)(TCNE)$ (2183 cm^{-1}), or of the bromo or iodo complexes $RhClX_2(Ph_3P)_2(t\text{-}BuNC)$ (X = Br, 2220 cm^{-1}, or X = I, 2205 cm^{-1}). Hence the electron density on the rhodium is in the order O_2 > TCNE > X_2. The high ν_{CN} suggests a high effective oxidation state of metal. This trend indicates that the effective oxidation state of rhodium in the O_2 complexes is not as high as those in the typical Rh(III) complexes such as $RhClX_2(Ph_3P)_2(t\text{-}BuNC)$. Therefore, the O_2 ligand is not properly regarded as an O_2^{2-} ion.

(c) **Electronic Spectra.**—All the dioxygen complexes described in this paper have poor solubility in many common solvents and only in CH_2Cl_2 are they sufficiently soluble to allow measurements of electronic spectra (Table II). In general, two strong, characteristic maxima in the ultraviolet region shift to a longer wavelength on the change of halogen ligand from chloride to iodide. These may be assigned as essentially charge-transfer bands from ligand to rhodium. A weak d–d band observable by reflectance spectra of the solid sample shows a similar trend (*cf.* Table II) on change of halogen ligand.

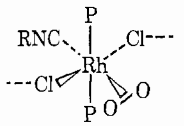
A remarkable spectral change occurs on dioxygenation of the parent complexes. The two maxima of **2a** are instantaneously replaced by a stronger absorption characteristic of the O_2 complex **1a** upon introduction of air, demonstrating the great affinity of **2a** toward dioxygen in dilute solution. In contrast, in the dry crystalline state only slow absorption of O_2 occurs, requiring prolonged contact with air (at least for a few months). Incidently the formation of the O_2 complex from the corresponding *p*-tolyl isocyanide derivative **2b** in dilute CH_2Cl_2 solution was traced by the spectra and found to proceed much less readily as compared with **2a**.

(d) **Structure.**—The isotopic ir study has shown[9] that the dioxygen ligand forms the "side-on" coordination similar to the Vaska's dioxygen complex. In order to obtain information about the relative orientation of two triphenylphosphine ligands in these complexes, 1,2-bis(diphenylphosphino)ethane (diphos) was used in place of two triphenylphosphine ligands. Reaction of $[RhCl(C_2H_4)_2]_2$ with diphos and *t*-BuNC gave an orange complex which did not yield a similar O_2 complex on attempted oxygenation. The reaction between **2a** and diphos yielded an orange semisolid from which the dioxygen complex **1a** containing triphenylphosphine slowly formed on exposure to air, and no dioxygen complex containing diphos was obtained. These results suggest a trans configuration of two phosphines in **1a** or **2a**. In an attempt to obtain further structural information, methyldiphenylphosphine was used in place of triphenylphosphine for the preparation of an analogous complex. The reaction of $[RhCl(C_2H_4)_2]_2$, first with methyldiphenylphosphine and then *t*-BuNC in benzene, readily evolved ethylene to give an orange solution with no crystal being formed. On exposure to air, it slowly gave a mixture of oxidation products containing methyldiphenylphosphine oxide, but no dioxygen complex was obtainable. An nmr investigation of the reaction mixture also indicated the presence of the phosphine oxide after exposure to air.

As mentioned above, the two phosphine or arsine ligands are probably in the trans position. There is a strong tendency for two triphenylphosphine ligands to be in mutually trans positions in many d^8 complexes of rhodium or iridium.[13] Assuming a pentacoordinate Rh(I) complex with the trans bisphosphine structure for the dioxygen complex, a possible structure for the unsolvated monomeric species just formed from **2** is shown below.



The insolubility of **1** in many organic solvents, including cold CH_2Cl_2, can be attributed to the intermolecular interaction in the solid state. This inference receives support from the electronic spectra which show some difference between the solid state (reflectance) and solution (*cf.* Table II). A broad band at 500–600 nm observed in the reflectance spectra of **1a–d** disappears in the solution (CH_2Cl_2). Visually the color changes from green to orange upon dissolution. The interaction may be caused by bridging of the anionic ligand such as a halogen or partially anionic oxygen molecule.[6a] The infrared Rh–Cl stretching value of 295 cm^{-1} of **1a** (R = *t*-Bu) is lower than that of the parent Rh(I) complex **2a** (312 cm^{-1}). As the oxidation state of the central metal is certainly raised to some extent on addition of dioxygen, the rise will increase the Rh–Cl stretching frequency. Many chlororhodium(III) complexes have the Rh–Cl stretchings in the region 300–330 cm^{-1}. However, the effect of the trans ligands is particularly marked.[14] The decrease in ν_{Rh-Cl} on dioxygenation may be the result of chloride bridging or the effect of the dioxygen ligand. Both effects could be operative. The closely related Vaska complex having ν_{Ir-Cl} at 317 cm^{-1} shows a slight decrease of ν_{Ir-Cl} on dioxygenation (314 cm^{-1}). A solution of **1a** in boiling CH_2Cl_2, $CHCl_3$, and PhCl, where ligation of these organic chlorides through their chlorine atom is possible, may be taken as support for the chloride-bridged structure. The appearance of one relatively sharp Rh–Cl stretching in all the chlororhodium–dioxygen complexes (**1a**, **c**, **g**) strongly suggests the trans position of two chloro ligands as shown above.



The solvated complex, *e.g.*, with CH_2Cl_2, may have a similar structure in which the solvent weakly coordinates trans to the chloro ligand. The instability of the solution of the dioxygen complexes can now be understood through the same reasoning as applied for the O atom transfer reactions in (dioxygen–isocyanide)nickel; *i.e.*, an attack of a donor increasing the back-donation to the O_2 ligand results in the rupture of the O–O bond causing an O-atom transfer.[7b] Indeed oxygenation of the phosphine ligands was observed in the decomposition products from **1a–c**.

Strength of Metal–Dioxygen Interaction.—Reappraisal of the existing methods for evaluating the strength of metal–dioxygen interaction or efforts to find new better methods have been important facets of research on dioxygen complexes. Reversibility of dioxygen addition, thermal decomposition points, infrared metal–dioxygen stretching data, and bond lengths around the metal–dioxygen system may be counted as such existing methods. Although each method suggests the relative order of strength of the interaction, the recent accumulation of various data is now beginning to indicate some inconsistency among the results obtained. The trend of metal–dioxygen stretching frequency (*cf.* Table II), *i.e.*, *t*-BuNC complex < *p*-tolyl complex, is not in accord with the trend observed in reversibility of dioxygen addition in **1a** and **1c**. The trend in that frequency with halogen triad (*cf.* Table II), *i.e.*, Cl > Br > I, is also contrary to that expected from the well-known reversibility in Vaska's iridium complexes. These data, though admittedly qualitative, suggest that the apparent reversibility is not thermodynamically controlled.[15] Recent findings of a remarkable ligand dependency[7a,16] of dioxygen uptake in various iridium–phosphine complexes suggest the importance of the steric effect in kinetically controlled processes. Thermal decomposition points of the chloro–rhodium complexes **1a–c** (*cf.* Table I) and also the apparent solution stability are in the order *t*-BuNC > *c*-C_6H_{11} > *p*-tolyl, which at the first sight may seem to be identical with the trend in the reversibility. However, when one realizes the thermal property to be a result of complex combination of several factors such as ligand oxidizability (*cf.* stability of the PPh_3 derivatives and the $AsPh_3$ derivative), lattice energy in the solid state, or solvation in solution, the observed trend thus cannot simply be related only to the metal–dioxygen bond. In view of the complexity of nature of the metal–dioxygen bond, a correlation of certain experimental data with the strength of such bonds appears to be more complex than originally believed. Therefore, more extensive research is necessary in order to further clarify the nature and extent of the chemical activation of coordinated dioxygen.

Experimental Section

Materials.—The following reagents were prepared according to literature methods: halogenotris(triphenylphosphine)rhodium,[17] methyl isocyanide,[18] cyclohexyl isocyanide,[19] *p*-tolyl isocyanide,[19] *tert*-butyl isocyanide.[20] The other more common reagents are all of extra pure grade. The ir and nmr spectra were measured with Hitachi Perkin-Elmer Model 225 and JEOL 4H-100 instruments, respectively. The electronic spectra were obtained with a Shimadzu MPS-50L and a Hitachi EPS-3T.

---

(13) W. P. Griffith, "The Chemistry of the Rarer Platinum Metals," Interscience, London, 1967.

(14) M. A. Bennett, R. J. H. Clark, and D. L. Milner, *Inorg. Chem.*, **6**, 1647 (1967).

(15) L. Vaska, L. S. Chen, and W. V. Miller, *J. Amer. Chem. Soc.*, **93**, 6671 (1971).

(16) G. R. Clark, C. A. Reed, W. R. Roper, B. W. Shelton, and T. N. Waters, *Chem. Commun.*, 758 (1971).

(17) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966).

(18) J. Casanova, R. E. Schuster, and N. D. Werner, *J. Chem. Soc.*, 4280 (1963).

(19) I. Ugi and R. Meyr, *Chem. Ber.*, **93**, 239 (1960).

(20) S. Otsuka, K. Mori, and K. Yamagami, *J. Org. Chem.*, **31**, 4170 (1966).

Elemental analysis was performed in our laboratory and also in the research laboratory of Japan Synthetic Rubber Ltd. Molecular weights were measured in chloroform by a Hitachi vapor pressure osmometer, Model 115. All the operations involving air-sensitive parent complexes, *e.g.*, $RhX(PPh_3)_2(RNC)$ or $RhX(PPh_3)_2(RNC)_2$, were performed under pure nitrogen. For brevity, only some typical examples of the preparation of the dioxygen complexes and parent compounds are described below.

(a) **Preparation of Dioxygen Complexes. Chloro(dioxygen)bis(triphenylphosphine)(*tert*-butyl isocyanide)rhodium, $RhCl(O_2)(PPh_3)_2(t\text{-}BuNC)$ (1a). Method a.**—A solution of chlorotris(triphenylphosphine)rhodium (0.43 mmol) in 5 ml of benzene was mixed with a benzene solution(1 ml) of *tert*-butyl isocyanide (35 mg, 0.43 mmol) and stirred under N_2 for 2 hr. A small amount of brown precipitate appeared upon addition of 2 ml of ethanol. The precipitate was filtered off to give a yellow solution, which yielded a green precipitate on standing in air for 30 min. These precipitates were collected by filtration and washed with benzene and ethanol; *ca.* 0.1 g of a yellowish green powder (30%) was obtained after drying under vacuum.

Method b.—The crystals or powder of **2a** was made wet with a small amount of benzene (*ca.* 0.5 ml) or dichloromethane and was finely ground in air. The color change from yellow to green occurred in *ca.* 1–2 min at room temperature. The solvent was allowed to evaporate yielding a green powder of the dioxygen complex: mol wt ($CHCl_3$), 732; calcd 778. Similar oxygenations can also be performed in other organic solvents. The sample prepared in CH_2Cl_2 contained 1 mol of CH_2Cl_2 after drying which is removable on prolonged standing in air.

Chloro(dioxygen)bis(triphenylphosphine)(cyclohexyl isocyanide)rhodium, $RhCl(O_2)(PPh_3)_2(c\text{-}C_6H_{11}NC)$ (1b).—The complex was prepared similarly as above (method a) using 0.4 g of $RhCl(PPh_3)_3$ and 47 mg of cyclohexyl isocyanide; 0.2 g (61%) of the green powder was obtained. The corresponding bromo complex was prepared similarly.

Chloro(dioxygen)bis(triphenylphosphine)(*p*-tolyl isocyanide)rhodium, $RhCl(O_2)(PPh_3)_2(p\text{-}CH_3C_6H_4NC)$ (1c).—On addition of 0.050 g of *p*-tolyl isocyanide in 1 ml of benzene to a stirred suspension of 0.4 g of chlorotris(triphenylphosphine)rhodium in benzene (9 ml), a deep orange solution resulted. After concentration of the solution to *ca.* one-third volume, the solution was exposed to air and allowed to stand overnight at room temperature. The color changed to deep brown and after concentration of the solution precipitation of a gray powder occurred. The precipitate was collected and washed well with a small amount of benzene and then with ethanol to give the dioxygen complex as a pale yellowish brown powder (0.2 g).

Bromo- or Iodo(dioxygen)bis(triphenylphosphine)(*tert*-butyl isocyanide)rhodium, $RhX(O_2)(PPh_3)_2(tBuNC)$, X = Br or I (1d and 1f).—These were prepared by method a or b. An example is described below. To a benzene suspension of 20 ml of iodotris(triphenylphosphine)rhodium (0.2 g, 2 mmol) was added with stirring a toluene solution of *tert*-butyl isocyanide (0.17 g, 2 mmol) under nitrogen. A red-brown homogeneous solution resulted immediately. Oxygen was then introduced and the solution was concentrated to *ca.* 10 ml under reduced pressure to give a greenish yellow precipitate. The precipitate was filtered in air, washed with ~2–3 ml each of *n*-hexane three times, and dried *in vacuo* (41% yield).

Chloro(dioxygen)bis(triphenylphosphine)bis(*tert*-butyl isocyanide)rhodium, $[Rh(O_2)(PPh_3)_2(t\text{-}BuNC)_2]Cl\cdot{}^1/_2CH_2Cl_2$ (1h).—Into a dichloromethane solution (15 ml) of $RhCl[P(C_6H_5)_3]_2(t\text{-}BuNC)_2\cdot C_6H_6$ (0.307 g, 0.338 mmol) was introduced oxygen under stirring at −70°; the mixture was kept for 2 days in a refrigerator. The initial yellow color turned to pale brown. The reaction mixture was concentrated below room temperature to give pale brown microcrystals (*ca.* 0.12 g) by addition of a small amount of toluene. The ir spectrum exhibited the expected ν_{NC} and ν_{RhO_2} bands; the ^1H nmr spectra (CH_2Cl_2) showed δ 0.62 and 0.92 (TMS) (1:1), (singlet, *t*-Bu), 7.57 ppm (multiplet, Ph). The conductivity in CH_2Cl_2 was 46.2 ohm^{-1} cm^2 mol^{-1} (at 25°, 3.72×10^{-1} mol $l.^{-1}$).

Chloro(dioxygen)bis(triphenylarsine)(*tert*-butyl isocyanide)rhodium, $RhCl(O_2)(AsPh_3)_2(t\text{-}BuNC)$ (1g).—$[RhCl(C_2H_4)_2]_2$ (0.10 g) and 1.0 g of Ph_3As were mixed, and 10 ml of ethanol was added. The yellow solution, containing an excess of undissolved arsine, was heated at 70–75° for 0.5 hr. The resulting yellow precipitate, $[RhCl(AsPh_3)_2]_2$, was filtered by suction in air, washed with ethanol, and dried *in vacuo*. *Anal.* Calcd for $C_{36}H_{30}AsClRh$: C, 57.59; H, 4.03; Cl, 4.72. Found: C, 55.25; H, 4.17; Cl, 5.32. This crude product was used to prepare the dioxygen complex as a green precipitate by treatment with an equimolar amount of a dilute benzene solution of *tert*-butyl isocyanide followed by aerial oxygenation.

(b) **Preparation of Parent Phosphine(isocyanide)rhodium(I). Chlorobis(triphenylphosphine)(*tert*-butyl isocyanide)rhodium, $RhCl(PPh_3)_2(t\text{-}BuNC)$ (2a).**—To a suspension of 0.95 g (1.03 mmol) of $RhCl(PPh_3)_3$ in 8 ml of toluene was added a stock solution of *t*-BuNC (87 mg, 1.05 mmol in 5.0 ml) in benzene with stirring. A yellow solution with red and orange precipitates resulted. The precipitates dissolved slowly giving a deep orange solution. After 30 min at room temperature the mixture was warmed to 50° for 15 min to give a deep orange solution containing a brown solid deposit. After cooling, the supernatant liquid was transferred to another Schlenk tube and concentrated under reduced pressure to *ca.* one-half volume (~6–7 ml); some crystals appeared. After standing overnight, a large amount of orange crystals formed; these were isolated by sucking out the deep orange solution in N_2 and washed with *ca.* 2 ml of toluene and dried under vacuum, yield 0.66 g (87%). The mother liquor was concentrated again to yield less pure crystals (*ca.* 0.02 g) and, on standing in air, yielded a small amount of green O_2 complex (1a).

Chlorobis(triphenylphosphine)(*p*-tolyl isocyanide)rhodium, $RhCl(PPh_3)_2(p\text{-}CH_3C_6H_4NC)$ (2b).—In a Schlenk-type flask, 0.45 g of $RhCl(PPh_3)_3$ (0.49 mmol) was placed, and 10 ml of benzene was added under nitrogen to give a red suspension. A benzene solution (1 ml) of freshly prepared and distilled *p*-tolyl isocyanide (0.05 g, 0.43 mmol) was added dropwise from a syringe. A color change to deep orange occurred upon mixing with dissolution of the starting material. The reaction mixture was concentrated *in vacuo* to *ca.* one-third volume until crystallization of orange product was induced. It took at least 2 days to complete the crystallization at room temperature. The well-formed orange needles were separated from the mother liquor and washed twice with benzene and dried *in vacuo* to give 0.160 g of **2b** (37%).

The mother liquor was exposed to air to give a grayish brown precipitate in *ca.* 2 hr. The precipitate was collected after standing overnight and washed well with benzene; 0.030 g of the dioxygen complex (1c) was thus obtained. From the dark filtrate triphenylphosphine oxide was isolated and identified by its ir spectrum after evaporation and crystallization.

2b is soluble in dichloromethane, chloroform, and benzene. The orange solution gradually darkens upon standing in air within 0.5 hr owing to formation followed by deterioration of the dioxygen complex: mol wt ($CHCl_3$ in air), 637; calcd 780.

Iodobis(triphenylphosphine)(*tert*-butyl isocyanide)rhodium, $RhI(PPh_3)_2(tert\text{-}BuNC)$ (2d).—The preparation was essentially identical with that for **1f** except without any treatment with oxygen. Bright yellow crystals (mp 148–149° dec) were obtained in good yield by concentrating the solution and allowing the reaction mixture to stand, ir (Nujol) 2100 cm^{-1} ($\nu_{C\equiv N}$). The bromo derivative **2c** was prepared in a similar manner by the reaction of bromotris(triphenylphosphine)rhodium with 1 molar equiv of *tert*-butyl isocyanide in benzene. Orange square plates formed on concentration of the deep orange solution *in vacuo* to *ca.* one-half volume followed by standing under nitrogen at room temperature for 1–2 days, ir (Nujol) 2095 cm^{-1} ($\nu_{C\equiv N}$).

Chlorobis(triphenylphosphine)bis(*tert*-butyl isocyanide)rhodium, $[Rh(PPh_3)_2(t\text{-}BuNC)_2]Cl\cdot C_6H_6$ (3a).—To a red suspension of chlorotris(triphenylphosphine)rhodium (1.04 g, 1.13 mmol) in benzene (37 ml) was added *tert*-butyl isocyanide (0.24 ml, 2.24 mmol) under stirring at ambient temperature. Yellow microcrystals were precipitated within 1 hr. After stirring for 5 hr, the crystals were filtered under nitrogen and washed with benzene. The yield was almost quantitative. The ir spectrum showed a strong band at 2120 cm^{-1} due to $\nu_{C\equiv N}$ and at 670 cm^{-1} due to crystalline benzene. The absence of any strong band in the Rh–Cl stretching region (270–350 cm^{-1}) suggests its salt-like character: conductivity (CH_2Cl_2) 42.8 ohm^{-1} cm^2 mol^{-1} (at 25°, 1.12×10^{-2} mol $l.^{-1}$); ^1H nmr (CH_2Cl_2) δ 0.57 ppm (TMS) (singlet, *t*-Bu), ~7.34–7.50 ppm (multiplet, Ph). To the above filtrate was introduced gaseous dioxygen to give a green dioxygen complex, $RhCl(O_2)(PPh_3)_2(t\text{-}BuNC)$ (**1a**), which was identified by elemental analysis and comparison of its ir spectrum and melting point. The bromo complex, $[Rh(PPh_3)_2(t\text{-}BuNC)_2]Br\cdot C_6H_6$ (**3b**), was similarly prepared from $RhBr(PPh_3)_3$, ir (Nujol) 2125 cm^{-1} ($\nu_{C\equiv N}$).

(c) **Preparation of the Tetracyanoethylene Complex. $RhCl(PPh_3)_2(t\text{-}BuNC)(TCNE)\cdot CH_2Cl_2$.**—The parent complex (2a, 40 mg) was mixed with an excess of TCNE in benzene, and the suspension was heated at 60–65° for 1 hr with stirring to give a yellow precipitate (30 mg) which was recrystallized from warm dichloromethane. The lemon yellow crystals were stable in air, ir (CH_2Cl_2) 2227 (for $\nu_{C\equiv N}$ of coordinated TCNE) and 2196 cm^{-1} (for $\nu_{C\equiv N}$ of *t*-BuNC).

(d) **Bromosulfatobis(triphenylphosphine)(*tert*-butyl isocyanide)(sulfur dioxide)rhodium, $RhBr(SO_4)(PPh_3)_2(t\text{-}BuNC)(SO_2)$ (5).**—When added to liquid sulfur dioxide, 1d readily reacted with it to give a yellow solution which on evaporation gave a yellow powder: ir (Nujol) 2200 ($\nu_{C\equiv N}$), 1265, 1150, 1030, 870, and 660 cm^{-1} (for coordinated SO_2[21] and SO_4^{2-}).

Acknowledgments.—The authors are indebted to Dr. M. A. Bennett, Australian National University, for helpful discussions and suggestions. Experimental assistance by Mr. M. Uno and Mr. Y. Tachibana and the oxygen analysis by Japan Synthetic Rubber Co. are most gratefully acknowledged.

[21] L. Vaska and S. S. Bath, *J. Amer. Chem. Soc.*, **88**, 1333 (1966).

CONTRIBUTION FROM THE WM. A. NOYES LABORATORY,
UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS 61801

Stabilization of High Oxidation States of Nickel with Pyridine Oxime Ligands

BY RUSSELL S. DRAGO* AND EVERETT I. BAUCOM[1]

Received January 10, 1972

In this article we report the preparation, isolation, and characterization of nickel(III) complexes with *syn*-2-benzoylpyridine oxime and *syn*-2-phenacylpyridine oxime. Various criteria are employed to establish the oxidation state of nickel. These findings are employed to extend and support a model reported earlier to account for the stability of a nickel(IV) complex of 2,6-diacetylpyridine dioxime.

Introduction

An earlier report from this laboratory[2] described the preparation and characterization of a nickel(IV) complex and suggested a model which described the ligand properties that stabilize the high oxidation state. Clearly, any models that attempt to explain how unusual oxidation states can be stabilized must be based on a semiempirical approach and consequently require the right input information. Incorrect input has given rise to many incorrect notions in this area.[3–9] In this article, we extend our earlier study on oxime ligands and provide evidence for the existence of a nickel(III) complex.

The literature is filled with reports of complexes which are claimed to be Ni(III), but subsequent work showed the claim to be incorrect. The potential difficulties in determining the oxidation state are exemplified in the work by Foust and Soderberg,[3] who showed that the complexes originally formulated as bromo- and iodobis(diphenylglyoximato)nickel(III) were in fact inclusion-like compounds of nickel(II) with halogen atoms sandwiched between layers of the planar bis(diphenylglyoximato)nickel(II). The observed epr spectra gave *g* values near 2.01. The halogen atoms apparently interacted with the phenyl rings of the complex rather than the metal, forming molecular inclusion complexes.

During the early to mid 1960's, a large number of dithiolate complexes, formulated as square-planar nickel(III), were reported.[4] Numerous later studies showed these complexes to be in fact cation-stabilized radical ligand compounds. In particular, Davidson, *et al.*,[5] showed that the ^{61}Ni hyperfine splitting in one of the "nickel(III)" dithiolate complexes amounted to only 4.5 G, indicating that little unpaired spin resided on the nickel atom. Numerous "nickel(III)" complexes similar to the dithiolates were shown to fit into the same overall pattern, as cation-stabilized radicals,[6] *e.g.*, paramagnetic[7] $[Ni(diars)_2Cl_2]Cl$ (diars = *o*-phenylenebis(dimethylarsine)), a series of complexes[8] $[Ni(diars)_2X_2]Y$ ($X^- = Br^-, SCN^-, I^-$; $Y^- = Br^-, SCN^-, I^-, ClO_4^-, {}^1/_2PtCl_6^{2-}$) ($\mu$ ranged from 1.88 to 1.96 BM), and a triarsinenickel(III) complex[9] $NiTBr_3$ $\{T = CH_3As[CH_2CH_2CH_2As(CH_3)_2]_2\}$. A recent study[10] showed the complex $Ni(diars)_2Cl_2^+$ to be best described as a nickel(II)-stabilized diarsine radical. The primary arguments supporting this description of the complex, as opposed to the nickel(III) designation, were *g* values (powder and frozen ethanol solutions) of 2.05, 2.09, and 2.14 with arsenic hyperfine splitting of 23 G. Furthermore, preliminary crystal data showed that the nickel–arsenic bond distance increased on oxidation of the parent nickel(II) complex.

Some of the more believable claims for nickel(III) complexes will be summarized. Klemm, Brandt, and Hoppe[11] reported the preparation of the violet complexes $K_n(Na)_{3-n}NiF_6$ by the fluorination of $K(Na)Cl-NiSO_4$ mixtures.

Curtis and Cook[12] claimed the isolation of two nickel(III) complexes containing the macrocycle

---

[1] Abstracted in part from the Ph.D. thesis of E. I. Baucom, University of Illinois, Urbana, Ill., 1970.

[2] E. I. Baucom and R. S. Drago, *J. Amer. Chem. Soc.*, **93**, 6469 (1971).

[3] A. S. Foust and R. H. Soderberg, *ibid.*, **89**, 5507 (1967).

[4] J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 49 (1968).

[5] A. Davidson, N. Edelstein, A. H. Maki, and R. H. Holm, *Inorg. Chem.*, **2**, 1227 (1963).

[6] A. L. Balch, F. Rohrscheid, and R. H. Holm, *J. Amer. Chem. Soc.*, **87**, 2301 (1965).

[7] R. S. Nyholm, *J. Chem. Soc.*, 2061 (1950); 2602 (1951); 2906 (1952); *Nature (London)*, **165**, 154 (1950).

[8] F. H. Burstall and R. S. Nyholm, *ibid.*, 3570 (1952).

[9] G. A. Barclay and R. S. Nyholm, *Chem. Ind. (London)*, 378 (1953).

[10] P. Kreisman, R. Marsh, J. R. Preer, and H. B. Gray, *J. Amer. Chem. Soc.*, **90**, 1067 (1968).

[11] W. Klemm, W. Brandt, and R. Hoppe, *Z. Anorg. Allg. Chem.*, **308**, 179 (1961).

[12] N. F. Curtis and D. F. Cook, *Chem. Commun.*, 962 (1967).