Reactions of Dioxygen Complexes of Nickel and Palladium

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Abstract: The reactions of dioxygen complexes $MO_2(t\text{-}BuNC)_2$ (M = Ni, Pd) with a variety of reagents including CO, CO_2, NO, N_2O_4, SO_2, C_6H_5NO, RCOX, Ph_3CBF_4, etc., have been investigated. In each case metal complexes and organic substances produced were isolated and characterized to show several types of reactions, *i.e.*, (1) atom-transfer redox reactions, (2) atom-transfer oxidation reactions, (3) oxidative substitution reactions, and (4) metal-assisted peroxidation reactions. The O–O bond is cleaved in reactions 1 and 2 while the bond is retained in reactions 3 and 4. Reactions of related complexes with molecular oxygen were also investigated. These results are interpreted in terms of the electronic properties of coordinated dioxygen and reactants.

Dioxygen complexes of low valent transition metals such as iridium,[1] rhodium,[2,3] platinum triad,[4,5] or ruthenium[6] have been known for several years. The nature of dioxygen–metal bonding in these complexes of "soft" metals has been a subject of a number of recent papers.[7-12] However, studies on their reactivities bearing on the bonding nature are rather sparse, most of the studies being devoted to the reactions of a platinum phosphine complex, $Pt(O_2)(PPh_3)_2$, with such molecules as CO,[11] CO_2,[11,13,18] NO,[14] NO_2,[14,15] SO_2,[15-17] CS_2,[18] acetone,[19,20] and other ketones.[20,21] In addition to these stoichiometric reactions, the catalytic oxidations of triarylphosphines[4,5] or alkylisocyanides[22] with platinum, palladium, or nickel complexes have been examined. The available data, most of which are of preliminary accounts, appear not to fully cover their reactivities, and the scattered information does not allow us to derive a consistent account of the chemistry. Previously we reported a few reactions of $M(O_2)(t\text{-}BuNC)_2$ (M = Ni, Pd; *t*-Bu = *tert*-butyl).[23] Now the study has been extended to cover a wide variety of reagents ranging from nucleophiles to electrophiles. One object of the present paper is to classify the types of reactions observed. Also investigated are reactions of free dioxygen with related complexes containing sulfur dioxide or nitrosobenzene as the ligand, *e.g.*, $ML(t\text{-}BuNC)_2$ (L = SO_2, C_6H_5NO). Another object of this paper is to find consistent interpretations for these reactions in terms of the activation of covalent molecules. The study is expected to increase our understanding of the role of metal for activation of dioxygen and related molecules.

Results

Various types of stoichiometric reactions of dioxygen ligand in the diamagnetic complexes MO_2L_2 may be classified into two broad categories with respect to whether the O–O bond is cleaved or maintained. We start with the reactions involving cleavage.

A reaction of $MO_2(RNC)_2$ (M = Ni, Pd; R = *tert*-butyl or cyclohexyl) with RNC takes place at room temperature leading to quantitative formation of a zerovalent complex $M(RNC)_n$ (n = 4 for M = Ni and 2 for Pd) and the corresponding isocyanate (eq 1). The

$$MO_2(RMC)_2 + \text{excess } RNC \longrightarrow M(RNC)_n + 2RNCO \quad (1)$$

reaction involves incipient formation of a labile isocyanate complex and subsequent facile replacement of the isocyanate ligand with the isocyanide.[23] The latter step, reductive substitution of an oxygenated product, is essential for the overall reaction using dioxygen to proceed catalytically.[22] This is a typical example for the "atom-transfer redox reaction" facilitated by a metal ion.[14]

Carbon monoxide reacts with $NiO_2(t\text{-}BuNC)_2$ at 20° in chlorobenzene affording not only CO_2 (eq 2) but also

$$NiO_2(t\text{-}BuNC)_2 + 4CO \longrightarrow Ni(CO)_2(t\text{-}BuNC)_2 + 2CO_2 \quad (2)$$

a substantial amount of *t*-BuNCO. Apparently the oxygen atoms are transferred to both CO and *t*-BuNC. In contrast to the reported reaction of $PtO_2(PPh_3)_2$ with CO, no carbonato complex could be detected; instead, the known stable nickel(0) complex $Ni(CO)_2(t\text{-}BuNC)_2$[24] was obtained. The low yield is due to isocyanate formation. Similarly, triphenylphosphine pro-

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(1) (a) L. Vaska, *Science*, **140**, 809 (1963); (b) L. Vaska and D. L. Catone, *J. Amer. Chem. Soc.*, **88**, 5324 (1966).

(2) (a) J. T. Mague and G. Wilkinson, *J. Chem. Soc. A*, 1736 (1966); (b) M. C. Baird, D. N. Lawson, J. T. Mague, J. A. Osborn, and G. Wilkinson, *Chem. Commun.*, 129 (1966).

(3) K. Hirota, M. Yamamoto, S. Otsuka, A. Nakamura, and Y. Tatsuno, *ibid.*, 533 (1968).

(4) S. Takahashi, K. Sonogashira, and N. Hagihara, *Nippon Kagaku Zasshi*, **87**, 610 (1966).

(5) G. Wilke, H. Schott, and P. Heimbach, *Angew. Chem.*, **79**, 62 (1967).

(6) K. R. Laing and W. R. Roper, *Chem. Commun.*, 568 (1968).

(7) R. Mason, *Nature (London)*, **217**, 543 (1968).

(8) J. A. McGinnety and J. A. Ibers, *Chem. Commun.*, 235 (1968).

(9) J. A. McGinnety, N. C. Payne, and J. A. Ibers, *J. Amer. Chem. Soc.*, **91**, 6301 (1969).

(10) J. Halpern, 11th International Conference on Coordination Chemistry, Haifa and Jerusalem, Israel, 1968 Plenary Lecture.

(11) J. P. Collman, *Accounts Chem. Res.*, **1**, 136 (1968).

(12) J. P. Collman, *Proc. Int. Conf. Coord. Chem., 12th*, 225 (1969).

(13) C. J. Nyman and G. Wilkinson, *Chem. Commun.*, 407 (1967).

(14) J. P. Collman, M. Kubota, and J. Hosking, *J. Amer. Chem. Soc.*, **89**, 4809 (1967).

(15) C. D. Cook and G. S. Jauhal, *ibid.*, **89**, 3066 (1967).

(16) R. W. Horn, E. Weissberger, and J. P. Collman, *Inorg. Chem.*, **9**, 2367 (1970).

(17) J. Valentine, D. Valentine, Jr., and J. P. Collman, *ibid.*, **10**, 219 (1971).

(18) P. J. Hayward, D. M. Blake, C. J. Nyman, and G. Wilkinson, *Chem. Commun.*, 987 (1969).

(19) R. Ugo, F. Conti, S. Cenini, R. Mason, and G. B. Robertson, *ibid.*, 1498 (1968).

(20) P. J. Hayward, D. W. Blake, G. Wilkinson, and C. J. Nyman, *J. Amer. Chem. Soc.*, **92**, 5873 (1970).

(21) P. J. Hayward and C. J. Nyman, *ibid.*, **93**, 617 (1971).

(22) S. Otsuka, A. Nakamura, and Y. Tatsuno, *Chem. Commun.*, 836 (1967).

(23) S. Otsuka, A. Nakamura, and Y. Tatsuno, *J. Amer. Chem. Soc.*, **91**, 6994 (1969).

(24) S. Otsuka, T. Yoshida, and Y. Tatsuno, *ibid.*, **93**, 6462 (1971).

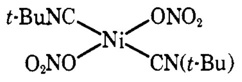
duces the known bisphosphine nickel(0) complex (30%)[23] and the phosphine oxide (eq 3); in this case the

$$NiO_2(t\text{-}BuNC)_2 + 4PPh_3 \longrightarrow Ni(PPh_3)_2(t\text{-}BuNC)_2 + 2Ph_3PO \quad (3)$$

formation of *t*-BuNCO was negligible. These reactions, though being accompanied by some minor side reactions, may also be regarded as examples of the atom-transfer redox reaction, since they involve displacement of oxygenated ligands with reactants.

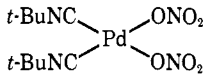
The next reaction pattern involves oxidation in the formal valency state of a metal together with formation of a stable anion attached to the metal upon oxygenation of a reactant such as N_2O_4, NO, CO_2, or SO_2. We propose to call this pattern an "atom-transfer oxidation reaction" to differentiate the state of the metal center from the above-mentioned redox reaction, although it is included in Collman's "atom-transfer redox reaction." Some of these reactions have precedent for platinum complexes.[11-20] Here we briefly comment on nickel and palladium derivatives.

$NiO_2(t\text{-}BuNC)_2 + N_2O_4 \longrightarrow$



(4)

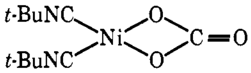
$PdO_2(t\text{-}BuNC)_2 + N_2O_4 \longrightarrow$



(5)

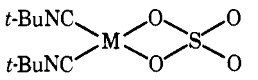
$$NiO_2(t\text{-}BuNC)_2 + 2NO + t\text{-}BuNC \longrightarrow [Ni(NO)(t\text{-}BuNC)_3]NO_3 \quad (6)$$

$NiO_2(t\text{-}BuNC)_2 + CO_2 + t\text{-}BuNC \longrightarrow$



$+\ t\text{-}BuNCO$ (7)

$MO_2(t\text{-}BuNC)_2 + SO_2 \longrightarrow$



M = Ni, Pd (8)

Both of the dioxygen nickel and palladium complexes react with N_2O_4 below −30° affording the dinitrato complexes quantitatively (eq 4 and 5). The reaction was rapid despite of the negligible dissociation[25] of N_2O_4 into NO_2 at the low temperature. It is interesting to observe different geometries for products from the two metals: trans and cis configuration for the nickel(II) and palladium(II) complex, respectively. The reaction of $PtO_2(PPh_3)_2$ with N_2O_4 was reported without experimental details to yield *cis*-$Pt(NO_3)_2(PPh_3)_2$.[14,15]

The versatility of nitric oxide as a ligand arising from its unusual electronic structure is well known.[26-29] No report, however, has been made on the reaction with dioxygen complexes apart from a paper[14] which mentioned formation of a *cis*-dinitro complex $Pt(NO_2)_2(PPh_3)_2$ from $PtO_2(PPh_3)_2$ without experimental details. We observed formation of a tetracoordinate complex (eq 6). The mechanism has not been studied and it is unknown whether the reaction involves a metal-catalyzed disproportionation of NO as was observed in the reaction with $Ni(CO)_4$[30] and $RhCl(CO)(PPh_3)_2$.[31]

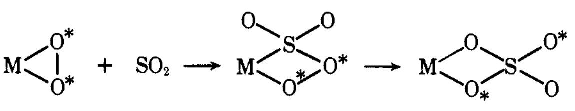
The reaction of CO_2 takes place below 0° affording a carbonato complex (eq 7) and a small amount of *t*-BuNCO. The reaction pattern (7) is quite analogous to the reported reaction of $PtO_2(PPh_3)_2$.[13] Later Hayward, *et al.*,[18] reported isolation of a percarbonato complex $Pt(CO_4)(PPh_3)_2$ from a reaction between $PtO_2(PPh_3)_2$ and CO_2 carried out in the presence of dioxygen; the percarbonato complex can be transformed into the carbonato complex. Isolation of a percarbonato complex from MO_2 $(t\text{-}BuNC)_2(M = Ni, Pd)$ was attempted without success.

A reaction of SO_2 with the diamagnetic dioxygen complexes ensues at −70° yielding *cis*-sulfato complexes (eq 8). We were able to prepare a mononuclear sulfur dioxide complex $Ni(SO_2)(t\text{-}BuNC)_3$ in which SO_2 ligates to the metal as a monodentate forming a *S*-sulfinate. The ir NC stretching frequencies[24] indicate a considerable electron transfer to the SO_2 ligand and suggest fairly strong coordination of the SO_2 ligand. Consistently the dissociation of SO_2 does not take place both in solution and in solid state even under vacuum. The reaction with dioxygen was examined; it takes place at −70° affording the same sulfato complex (eq 9). We

$$Ni(SO_2)(t\text{-}BuNC)_3 + O_2 \longrightarrow Ni(SO_4)(t\text{-}BuNC)_2 + t\text{-}BuNC \quad (9)$$

were unable to prepare an analogous sulfur dioxide complex for palladium; instead, we obtained a complex "$Pd(SO_2)(t\text{-}BuNC)_2$" in which the SO_2 ligands act as a bidentate bridging the two metals.[31a] To our surprise the complex was found to be quite inert to air oxidation. The difference in reactivity toward dioxygen will be discussed separately. We believe that these results are suggestive of primary importance of the coordination (hence hybridization) around the sulfur atom in determining the reactivity.

When sulfur dioxide attacks a dioxygen complex as a strong electrophile (electron affinity, 2.80 eV/mol[32]), it will reduce the electron density on the metal leading to weakening of the M–O_2 bond with retention of the O–O bond order. The latter has been reduced from its value in free dioxygen by coordination (see Discussion). This view finds support in reaction 8 indicating the absence of the oxygen–oxygen bond cleavage and is compatible with a reaction scheme (eq 10) proposed by Collman[16,17] for the formation of a *cis*-sulfato complex. It seems to have been established that sulfur dioxide attacks one of the M–O bonds but not the O–O bond.



(10)

The oxidation of nitrosobenzene with the dioxygen complex in the presence of 1 mol of free *t*-BuNC at −10–0° produces a nitrobenzene complex (eq 11). In

$$NiO_2(t\text{-}BuNC)_2 + C_6H_5NO + t\text{-}BuNC \longrightarrow \text{"}Ni(C_6H_5NO_2)(t\text{-}BuNC)_2\text{"} + t\text{-}BuNCO \quad (11)$$

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(25) P. J. Durrant and B. Durrant, "Advanced Inorganic Chemistry," Longmans, Green and Co., London, 1962, p 671.

(26) B. F. G. Johnson and J. A. McCleverty, *Progr. Inorg. Chem.*, **7**, 277 (1966).

(27) D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, **8**, 1282 (1969), and references therein.

(28) B. A. Freng, J. H. Enemark, and J. A. Ibers, *ibid.*, **8**, 1288 (1969).

(29) J. Masek, *Inorg. Chim. Acta*, **3**, 99 (1969).

(30) R. D. Feltham, *Inorg. Chem.*, **3**, 121 (1964).

(31) W. B. Hughes, *Chem. Commun.*, 1126 (1969).

(31a) NOTE ADDED IN PROOF. A recent X-ray analysis indicates the compound to be a trinuclear complex in which each SO_2 molecule bridges two Pd atoms.

(32) V. I. Vedeneyev, *et al.*, "Bond Energies, Ionization Potentials, and Electron Affinities," E. Arnold Ltd., London, 1966, p 196.

the absence of free *t*-BuNC the reaction produced intractable substances. Reductive substitution of the nitrobenzene ligand with *t*-BuNC or C_6H_5NO does not take place. Surprisingly the nitrobenzene complex is even stable to air. The strong coordination of nitrobenzene to the metal system is responsible for the failure in catalytic oxidation of nitrosobenzene with gaseous dioxygen. Dioxygen and nitrobenzene differ considerably in their affinity for the metal (*vide infra*); this also constitutes an unfavorable factor for the catalytic reaction taking place in one metal atom.

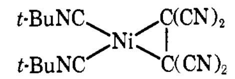
In order to examine the reactivity of a coordinated nitroso group we have prepared a series of novel nickel complexes $Ni(p\text{-}XC_6H_4NO)(t\text{-}BuNC)_2$ (X = H, CH_3, Cl, etc.), in which the nitroso group forms a triangular structure with the metal.[33] Displacement of the nitrosobenzene ligand with dioxygen occurred when a poor solvent like *n*-hexane was chosen for the reaction (eq 12). Similar displacement of a ligand leading to the dioxygen complex was observed for $Ni(C_6H_5C{\equiv}CC_6H_5)(t\text{-}BuNC)_2$ and $Ni(CS_2)(t\text{-}BuNC)_2$. The result (eq 12),

$$Ni(C_6H_5NO)(t\text{-}BuNC) + O_2 \longrightarrow NiO_2(t\text{-}BuNC)_2 + C_6H_5NO \qquad (12)$$

however, appears at first sight peculiar in view of reaction 11. It is accounted for by the lack of reactivity of the solid complex $NiO_2(t\text{-}BuNC)_2$ which precipitates out in the reaction system; the formation of nitrobenzene was detected in the reaction of the nitrosobenzene complex with dioxygen carried out in chlorobenzene which dissolves the dioxygen complex. As nitrosobenzene is unable to substitute the nitrobenzene ligand, the type of reaction 11 may also be termed as an "atom-transfer oxidation reaction."

Now we come to an extreme case where an enhanced drainage of electron density from the metal to an attacking electrophile leads to the M–O_2 bond cleavage releasing dioxygen. Examples are the reactions with halogens or strong electrophiles like tetracyanoethylene (TCNE),[23] which may be classified as an "oxidative substitution reaction." The substitution with TCNE (eq 13) is incomplete and the oxygen atom transfer to *t*-BuNC ligands producing *t*-BuNCO is inevitable, a result reasonable in view of the comparable dπ-accepting

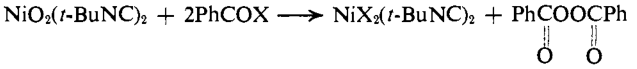
$$NiO_2(t\text{-}BuNC)_2 + (NC)_2C{=}C(CN)_2 \longrightarrow$$



$$+ \; O_2 \qquad (13)$$

properties of TCNE and O_2.[24,34]

The last type is the reaction with a carbonium ion or a similar electrophile leading to the peroxidation of reagents. For example, benzoyl bromide reacts with the dioxygen complex instantaneously at −78° affording benzoyl peroxide and the metal halide complex in good yields (eq 14). Benzoyl chloride gave the peroxide in a



$$NiO_2(t\text{-}BuNC)_2 + 2PhCOX \longrightarrow NiX_2(t\text{-}BuNC)_2 + Ph\underset{\underset{O}{\|}}{C}O\,O\underset{\underset{O}{\|}}{C}Ph$$

$$X = Cl, Br \qquad (14)$$

smaller yield. In the absence of the complex the peroxidation of PhCOCl with gaseous dioxygen does not, of course, take place. A similar facile peroxidation takes place at low temperature with triphenylmethyl bromide or tetrafluoroborate (eq 15). The reaction of

$$NiO_2(t\text{-}BuNC)_2 + 2Ph_3CX \longrightarrow Ph_3COOCPh_3 + NiX_2(t\text{-}BuNC)_2$$
$$X = Br, BF_4 \qquad (15)$$

trityl halide or cation with gaseous dioxygen does not yield the peroxide in an appreciable amount. In these reactions (eq 14 and 15) dioxygen liberation was not observed in contrast to the oxidative substitution reaction (eq 13), which is effected also by strong electrophiles. An attempt to react hexaphenylethane with $NiO_2(t\text{-}BuNC)_2$ in nitrogen atmosphere carried out similarly failed to give the peroxide, hexaphenylethane being recovered unchanged, a result suggestive of the reluctance toward radical attack. These processes, which may be termed as "metal-assisted electrophilic peroxidations," represent the first reported examples for successful peroxidations of organic moieties with transition metal–dioxygen complexes.

Characteristics of Complexes. We were able to characterize most of the new complex products described in the foregoing section primarily on the basis of elemental analysis (Table I) and ir (Table II) and nmr data (Table III). They are all diamagnetic except for the sulfato–nickel(II) complex.

The nonelectrolytic, sparingly soluble *sulfato complexes* $MSO_4(t\text{-}BuNC)_2$ (M = Ni(II), Pd(II)) show ir absorptions consistent with a cis-chelated sulfato structure quite analogous to the platinum complex $PtSO_4(PPh_3)_2$.[16,17] Thus the two intense NC stretching bands clearly indicate a cis arrangement of the two isocyanide groups and SO stretching bands contain three bands in each region of 1170–1010 (ν_3) and 680–580 cm^{-1} (ν_4) in accord with the C_{2v} local symmetry of a cis-chelated sulfato group.[16] The palladium(II) complex is diamagnetic, whereas the nickel(II) complex is paramagnetic with a magnetic moment μ_{eff} of 0.93 BM and a Weiss constant θ of +0.06°. Consistently the latter complex shows a broad nmr signal for the *tert*-butyl protons; the paramagnetic shift is rather small (Table III).

Bisnitrato complexes of the two metals differ distinctly in the ir NC stretching absorptions; on the basis of the sharp, symmetrical absorption a trans configuration is highly probable for the nickel(II) complex, whereas the two bands suggest a cis structure for the palladium(II) complex. The nitrate bands of the latter resemble those of bisnitrato complexes, $Co(NO_3)_2(OPPh_3)_2$[35] and $Ni(NO_3)_2(OPPh_3)_2$,[35] in which the nitrate groups coordinate to metal as monodentate ligands. The two bands in 1500-cm^{-1} region are then assignable to the asymmetric NO_2 stretchings and a band in the 1275-cm^{-1} region to the symmetric NO_2 stretching, a band at 989 cm^{-1} to the NO stretching, and a band at 820 cm^{-1} to the nonplane deformation.[35] The *trans*-nitratonickel(II) complex shows the nitrate bands at 1510, 1298–1275, 1013–1020, and 810 cm^{-1} regions. Comparable nitrate bands were observed for *cis*-$Pt(NO_3)_2(PPh_3)_2$.[14,15] The ^1H nmr (in CH_2Cl_2) shows a broad singlet for the *tert*-butyl protons; the reason for the broadness has not been investigated. It is not due to the paramagnetism as indicated by a sharp resonance for the methylene protons of the solvent. Due to its ex-

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[33] S. Otsuka and T. Yoshida, to be published.

[34] W. H. Baddley, *J. Amer. Chem. Soc.*, 90, 3705 (1968).

[35] E. Bannister and F. A. Cotton, *J. Chem. Soc.*, 2276 (1960).

Table I. Analytical and Some Physical Data

	Complex	Color	Mp, °C[a]	λ Ω^{-1} cm^2 M^{-1}	Calcd, % C	H	N	Found, % C	H	N
(I)	$Ni(C_6H_5NO_2)(t\text{-}BuNC)_2$	Reddish brown	117–120		55.21	6.66	12.03	56.07	7.02	11.94
(II)	$Ni(SO_2)(t\text{-}BuNC)_3$	Dark red	138–140		48.46	7.26	11.30	47.97	7.10	10.83
(III)	$Ni(SO_4)(t\text{-}BuNC)_2$	Pale brown	110–112	3.1	37.42	5.61	8.73	37.36	5.88	8.56
(IV)	$[Ni(NO)(t\text{-}BuNC)_3](NO_3)$	Dark purple	85–88	36.3	45.03	6.76	17.51	44.67	6.92	17.59
(V)	$Ni(NO_3)_2(t\text{-}BuNC)_2 \cdot H_2O$	Emerald green	87–88		32.73	5.49	15.27	32.10	5.08	15.36
(VI)	$Ni(CO_3)(t\text{-}BuNC)_2 \cdot H_2O$	Brown	130	1.8	43.74	6.64	9.25	43.62	6.21	8.75
(VII)	$[Pd(SO_2)(t\text{-}BuNC)_2]_2$[b]	Orange yellow	175–180		35.67	5.93	8.31	35.99	5.08	8.00
(VIII)	$Pd(SO_4)(t\text{-}BuNC)_2$	Pale brown	93–94		32.57	4.91	7.59	33.15	5.48	7.93
(IX)	$Pd(NO_3)_2(t\text{-}BuNC)_2$	Cream yellow	100–102		30.28	4.57	14.13	30.83	4.73	14.33

[a] All melting points with decomposition. [b] See ref 31a.

Table II. Infrared Frequencies of Complexes (cm^{-1})[a]

	Complex	ν_{NC}	Other bands
(I)	"$Ni(C_6H_5NO_2)(t\text{-}BuNC)_2$"	2160 vs	1590 m, 1524 w, 1488 m, sh, 1460 w, sh, 1425 s, 1377 s, br, 1355 w, sh, 1348 m, 1310 vw, 1208 w, sh, 1195 vs, 965 s, 851 vw, 760 w, sh, 755 s, 702 s, 693 s
(II)	$Ni(SO_2)(t\text{-}BuNC)_3$	2155 s 2120 vs 2115 vs	1398 vw, 1370 s, 1240 sh, 1230 s, 1208 vs, 1200 sh, 1060 vs, 870 vw, 735 vw, 725 vw
(III)	$Ni(SO_4)(t\text{-}BuNC)_2$	2210 vs 2150 vs	1400 vw, 1312 m, 1230 vs, br, 1170 vs, br, 1090 vs, 1010 vs, 989 s, 958 vs, 858 s, 770 vw, 715 m, 678 vs, 605 vs, 589 vs
(IV)	$[Ni(NO)(t\text{-}BuNC)_3](NO_3)$	2218 vs 2200 vs	1828 vs, br, 1407 vw, 1403 vw, 1345 vs, br, 1240 m, 1185 s, 841 w, 832 m, 712 w
(V)	$Ni(NO_3)_2(t\text{-}BuNC)_2 \cdot H_2O$	2253 vs	3300 vw, br, 1655 w, br, 1510 m, sh, 1400 vw, 1317 s, br, 1298 s, br, 1275 s, br, 1265 m, sh, 1236 w, 1185 s, 1013 s, 1020 s, 844 w, 813 w, sh, 810 m, 808 m, 756 w, 723 m
(VI)	$Ni(CO_3)(t\text{-}BuNC)_2 \cdot H_2O$	2240 vs 2230 vs	3300 m, br, 1695 vs, br, 1685 vs, br, 1680 vs, br, 1560 m, br, 1260 vs, 1238 m, 1195 vs, 996 s, 848 w, 817 w, 783 m, 763 w, 727 w
(VII)	$[Pd(SO_2)(t\text{-}BuNC)_2]_2$[b]	2170 vs 2155 vs	1398 vw, 1479 sh, 1235 m, sh, 1213 m, sh, 1202 vs, 1057 sh, 1048 vs, 920 m, br, 860 w, 742 m, 724 w, 700 w
(VIII)	$Pd(SO_4)(t\text{-}BuNC)_2$	2255 vs 2240 vs	1292 vs, 1250 s, 1240 s, 1190 vs, 1169 vs, 1123 vs, 1045 w, 980 s, 940 w, 880 m, 867 m, 840 vw, 738 w, 668 s
(IX)	$Pd(NO_3)_2(t\text{-}BuNC)_2$	2260 vs 2245 vs	1510 s, sh, 1495 vs, 1377 m, 1286 vs, br, 1276 vs, br, 1260 sh, 1233 m, 1195 m, 998 sh, 989 vs, 850 w, 820 m, 793 m, 735 w, br, 725 w, br, 710 w

[a] Measured in Nujol mull. [b] See ref 31a.

Table III. Nmr Data[a] for Complexes

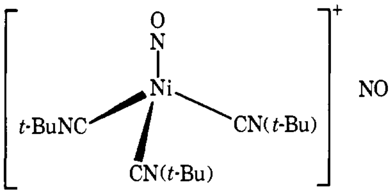
	Complex	τ (*tert*-butyl protons)[b]
(I)	$Ni(C_6H_5NO_2)(t\text{-}BuNC)_2$	8.05,[c] 8.79[c]
(II)	$Ni(SO_2)(t\text{-}BuNC)_3$	9.05[d]
(III)	$Ni(SO_4)(t\text{-}BuNC)_2$	9.0[e]
(IV)	$[Ni(NO)(t\text{-}BuNC)_3](NO_3)$	8.40
(V)	$Ni(NO_3)_2(t\text{-}BuNC)_2 \cdot H_2O$	8.25[f]
(VI)	$Ni(CO_3)(t\text{-}BuNC)_2 \cdot H_2O$	8.65
(VII)	$[Pd(SO_2)(t\text{-}BuNC)_2]_2$[g]	8.48
(VIII)	$Pd(SO_4)(t\text{-}BuNC)_2$	8.48
(IX)	$Pd(NO_3)_2(t\text{-}BuNC)_2$	8.45

[a] Measured in CH_2Cl_2 unless otherwise stated, using TMS as internal reference at room temperature. [b] The observed resonance, unless otherwise stated, is a sharp singlet. [c] Broad signals of about equal intensity. In addition to these resonances, complex signals centered at τ 2.7 and 3.1 are observed and assigned to the aromatic protons. [d] Measured in benzene. [e] Very broad. [f] A broad signal with a half-height width of 32 Hz. [g] See ref 31a.

tremely hygroscopic nature, the anhydrous form could not be obtained in a state of analytical purity.

The *carbonato complex* $Ni(t\text{-}BuNC)_2CO_3$ was not obtained in an anhydrous form. The nonelectrolytic carbonato monohydrate shows three ir CO stretching bands which are in accord with the expected ir active modes (two A_1 and one B_2) for the bidentate CO_3^{2-} ligand (C_{2v}).[36] Similar bands were observed in $Pt(CO_3)(PPh_3)_2$[11,13] and a bidentate ligation was deduced for the carbonate ligand.

The dark purple, 1:1 electrolytic *nitrosyl complex* $[Ni(NO)(t\text{-}BuNC)_3]NO_3$ is soluble in polar organic solvents and shows a well-defined ^1H nmr spectrum (in CH_2Cl_2) implying diamagnetism. The equivalence of the protons of three *t*-BuNC ligands and the two strong ir NC stretching bands at 2200 and 2210 cm^{-1} are consistent with the local C_{3v} symmetry. The strong band at 1825 cm^{-1} is assignable to the NO stretching of the nitrosyl ligand, and the two bands at 1345 and 830 cm^{-1} are ascribed to the nitrate group, as the latter two bands disappear upon anion exchange with BPh_4^-, leaving the other bands essentially unaltered. Thus the complex appears to be of C_{3v} geometry with a nitrosyl ligand in the apical position and with the nitrato anion outside of the first coordination sphere. The NO stretching frequency of the nitrosyl ligand lies in a region found in low valent cobalt, nickel, and other group VIII transition metal complexes.[26]



The *nitrobenzene complex* of formula $Ni(C_6H_5NO_2)(t\text{-}BuNC)_2$ is polymeric material even in a solvent such as nitrobenzene. The ^1H nmr spectrum shows two resonances of equal intensity for the *tert*-butyl protons. One sharp ir NC stretching band was observed in Nujol

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(36) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed, Wiley-Interscience, New York, N. Y., 1970, p 169.

mull or in solution (nitrobenzene). The spectroscopic data alone are not sufficient to derive an unambiguous structural assignment and the elucidation requires an X-ray analysis. Eventually, we were able to obtain a discrete molecule $Ni(C_6H_5NO_2)_2(PPh_3)_2$ which forms well-developed brown crystals[37] and the X-ray analysis has been undertaken. It may be noted that the NC stretching frequency[24] reflects the dπ-acceptor property of nitrobenzene rationalizing the propensity to form a strong coordination bond to a nickel(0) species.

Discussion

Coordinated dioxygen behaves differently from the free paramagnetic molecule in many respects. Enhanced reactivity of the dioxygen ligand of the low-spin complexes MO_2L_2 is apparent from the results described above. We intended to have a quantitative measure describing the degree of activation of dioxygen molecule upon coordination. There are a number of physical or chemical properties, each specifically adapted for the molecule in excited states which could be used as the measure. Physical characteristics and specific reactions of the lowest singlet state ($^1\Delta_g$) have been extensively studied.[38,39] A few attempts were made to find such a measure for coordinated molecules. The O–O bond lengths in dioxygen complexes vary over a wide range, from 1.31 to 1.62 Å,[9] and this last distance points out the inadequacy of the description only in terms of O_2^{n-} (n = 1 or 2) for this type of complex. The values of O–O stretching force constants are also lower than that of O_2^{2-} ion (Table IV). These implications, however, do not exclude the partially negative nature of the dioxygen ligand. Citing some of the structural data on complexes containing carbon disulfide, acetylene, butadiene, and oxygen molecule, Mason[7] regards the perturbation in electronic structure of a coordinated molecule as such that the wave function describing the bonding in the metal complexes will contain functions representing excited states of both the metal and ligands. The degree of mixing strongly depends on the metal and the other ligands. A "perketyl" metal was obtained from reaction of $PtO_2(PPh_3)_2$ and acetone (eq 16), and Ugo, *et al.*,[19] have suggested mixing of an excited state $^3\Sigma_u^-$ assuming that the ketone group directly inserts into the polarized O–O bond. The various chemical measures are not as directly as informative as they might appear. The above argument made by Ugo, *et al.*, is only tenable provided the assumption regarding the reaction path is valid.

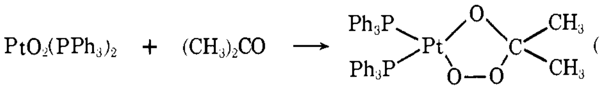
(16)

Table IV. Force Constant and Bond Length Data of Dioxygen in Various States

States	Example	Force constant f_{O-O}, mdyn/Å[a]	Bond length, Å[b]
Coordinated	$PtO_2(PPh_3)_2$	3.0[c]	1.45[d]
Excited	$NiO_2(t\text{-}BuNC)_2$	3.5[c]	
	$^3\Sigma_u^-$	2.3	1.60$_4$
	$^3\Sigma_u^+$	3.2	[1.41]
	O_2 $^1\Sigma_g^+$	9.68	1.22$_7$
	$^1\Delta_g$	10.8	1.21$_5$
	$^3\Sigma_g^-$	11.5	1.20
Anionic	KO_2	6.2[e]	1.28[f]
	Na_2O_2	5.5[e]	1.49[f]

[a] The force constants for O_2 were calculated using the electronic band spectra cited by G. Herzberg, "Spectra of Diatomic Molecules," Vol. I, 2nd ed, Van Nostrand, Princeton, N. J., 1950, p 559. [b] From the above reference, pp 559–560. [c] Reference 40. [d] Taken from the value reported by Kasai, *et al.* [T. Kashiwagi, N. Yasuoka, N. Kasai, and M. Kakudo, *Chem. Commun.*, 743 (1969)]. This value seems more reasonable than 1.26 Å reported by Cook, *et al.* [C. D. Cook, P.-T. Cheng, and S. C. Nyburg, *J. Amer. Chem. Soc.*, **91,** 2123 (1969)]. [e] F. J. Blunt, P. J. Hendra, and J. R. Mackenzie, *Chem. Commun.*, 278 (1969). [f] N.-G. Vannerberg, *Progr. Inorg. Chem.*, **4**, 125 (1962).

We have carried out ^{18}O-isotopic infrared studies for the complexes $PtO_2(PPh_3)_2$ and $M(O_2)(t\text{-}BuNC)_2$ (M = Ni, Pd) and calculated the approximate force constants, f_{O-O} (a_1) and f_{M-O} (a_1 and b_1), on the basis of a simple triatomic isosceles local model. The details being given elsewhere,[40] only some force constants values are reproduced in Table IV together with the O–O bond length data. The force constants f_{O-O} found for $NiO_2(t\text{-}BuNC)_2$ and $PtO_2(PPh_3)_2$ are comparable with those of higher excited states.[41]

The low force constants are in qualitative agreement with the reactivity of dioxygen ligand. The O–O bond cleavage reactions (eq 1–3) would then be accounted for with the increase in electronic population in the π^* orbital effectuated by ligation of an electron-donating reactant. From these reactions as well as the physical parameters we expected peroxidation of conjugated dienes, a characteristic reaction of $^1\Delta_g$ dioxygen, or epoxidation of olefins which may be achieved with an oxygen atom (^1D) derived from the highest excited state $^3\Sigma_u^-$ of the dioxygen molecule.[42] Despite our numerous attempts with these peroxo complexes, we have failed so far to find a reaction manifesting one of these behaviors.

When the reactant is an electrophile, the reduction in electron density in metal (hence in the dioxygen ligand) would not favor the O–O bond cleavage. Indeed we observed retention of the O–O bond upon the attack of an electrophile (eq 13–15). An extreme case is the attack of a halogen molecule which results in a complete reverse flow of electronic populations from a dioxygen ligand to the reagent. This view also accounts for the similar reaction (eq 13) partially effected by tetracyanoethylene. These oxidative substitution reactions are found for the electrophile which does not have strong affinity for the oxygen atom or molecule.

The atom-transfer oxidation reactions (eq 4–8) or the peroxidations (eq 14, 15) were observed for an electrophile which has some propensity to form bonds with oxygen. An example for attack of 1 mol of such an electrophile is the reaction of sulfur dioxide with a di-

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(37) S. Otsuka and Y. Tatsuno, to be published.

(38) R. P. Wayne, *Advan. Photochem.*, 7, 311 (1969).

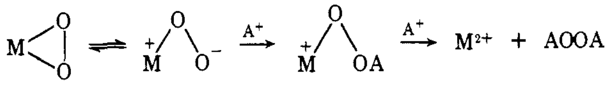
(39) D. R. Kearns, *J. Amer. Chem. Soc.*, **91**, 6554 (1969).

(40) A. Nakamura, Y. Tatsuno, M. Yamamoto, and S. Otsuka, *ibid.*, **93**, 6052 (1971).

(41) As suggested by a referee, treatment of coordinated dioxygen as a perturbed or partly negative discrete oxygen molecule is not rigorously permissible. The whole metal–dioxygen system must be considered for complete understanding.

(42) R. J. Cvetanovic, *Advan. Photochem.*, **1**, 115 (1963).

oxygen complex, for which a reasonable mechanism (eq 10) was proposed by Collman, *et al.*[16,17] When 2 mol of electrophiles participates in the reaction, then two reaction paths are possible for the attack, either a concerted or a successive one. A theory of vibrationally induced perturbation in molecular electron distribution[43-46] predicts that since the asymmetric vibrational mode b_1 of the local MO_2 isosceles is consonant with the transition density[43b] of B_1 symmetry derived from the representations for the ground state (A_1) and one of the excited state (B_1),[47] the asymmetric stretching vibration will assist the transition to the excited state, thus favoring an asymmetric rupture of the MO_2 triangle. The symmetry-allowed, vibrationally assisted unimolecular transition to a monodentate species provides a favorable pathway for the electrophilic attack.



Experimental Section

All reactions were performed under nitrogen atmosphere. Instruments for spectral measurements are the same as before.[23] Analytical data and physical data for complexes have been given in Tables I–III.

Materials. The gaseous compounds such as O_2, CO_2, NO, and SO_2 are commercial products of reagent grade and used without further purification. Carbon monoxide of reagent grade was used after passing through granular calcium dichloride and sodium hydroxide pellets. Pure dinitrogen tetraoxide was obtained by vaporizing the solidified sample. Triphenylmethyl tetrafluoroborate was prepared according to established procedures.[48] Preparation of isocyanide complexes of nickel and palladium and the corresponding dioxygen complexes employed here have been described before.[23]

I. Reaction of Dioxygen Complexes. (a) With Carbon Monoxide. Carbon monoxide was bubbled into a solution of 0.257 g (1 mmol) of $Ni(O_2)(t\text{-}BuNC)_2$ in 25 ml of chlorobenzene at −30° for 9 hr and subsequently at 20–30° for 2 hr. The pale green color of the solution turned to brown. The outlet gas from the reaction mixture was led to a small tube containing solid sodium hydroxide powder which trapped 1.076 g (1.28 mmol) of carbon dioxide. Vacuum distillation of the above brown solution afforded 0.52 mmol of *t*-BuNCO (identified and weighed as $(t\text{-}BuNH)_2CO$). The residue was extracted with *n*-hexane to give colorless needles (0.055 g, 0.20 mmol) which after sublimation [50–60° (2 mm)] was identified as $Ni(t\text{-}BuNC)_2(CO)_2$, mp 54–55°, by comparing its ir spectrum with that of an authentic sample.

(b) With Nitrosobenzene. To a chlorobenzene solution (30 ml) of 0.257 g (1 mmol) of $Ni(O_2)(t\text{-}BuNC)_2$ was added, in the presence of 1 mmol of free *t*-BuNC, 0.461 g (4.3 mmol) of nitrosobenzene at −10°. The brown reaction mixture, being allowed to stand overnight in a refrigerator, was subjected to vacuum distillation isolating *t*-BuNCO (0.63 mmol) which was weighed as $(t\text{-}BuNH)_2CO$. The residue from the above distillation was extracted with toluene, and the concentrated extract was treated with *n*-hexane affording reddish brown precipitates, mp 123–125° dec, whose ir spectrum was identical with that of the nitrobenzene complex, $Ni(C_6H_5NO_2)(t\text{-}BuNC)_2$, obtained from $Ni(t\text{-}BuNC)_4$ and $C_6H_5NO_2$. The yield was 0.268 g (0.77 mmol). The molecular weight (cryoscopic in nitrobenzene) showed polymeric structures (found, 3254; calcd for monomer, 348). In the absence of free *t*-BuNC, the reaction of $Ni(O_2)(t\text{-}BuNC)_2$ with C_6H_5NO gave unidentifiable brown polymeric substances.

(c) With Dinitrogen Tetraoxide. To a dichloromethane solution (25 ml) of 0.261 g (1.02 mmol) of $Ni(O_2)(t\text{-}BuNC)_2$ was introduced gaseous dinitrogen tetraoxide at −30° for 3 hr. The initially green solution immediately turned into a pale blue solution. After filtration the solution was concentrated and treated with *n*-hexane affording quantitatively emerald green, very hygroscopic crystals of formula $Ni(NO_3)_2(t\text{-}BuNC)_2H_2O$, mp 87–88° dec.

Similarly, 0.35 g (1.03 mmol) of $Pd(O_2)(t\text{-}BuNC)_2$ was treated with N_2O_4 in dichloromethane (20 ml) at −70 to −30° to give a pale yellow solution from which was isolated with *n*-hexane 0.361 g (91%) of creamy yellow crystals of formula $Pd(NO_3)_2(t\text{-}BuNC)_2$, mp 100–102° dec.

(d) With Nitric Oxide. To a dichloromethane (25 ml) solution containing 0.257 g (1.07 mmol) of $Ni(O_2)(t\text{-}BuNC)_2$ and 1 mmol of *t*-BuNC was introduced gaseous nitric oxide at −30°. The reaction mixture, being allowed to attain the ambient temperature during 3 hr, turned into a reddish purple solution. It was filtered, concentrated, and treated with a mixture of ether and *n*-hexane (1:1) to isolate 0.369 g (86%) of dark purple, very hygroscopic crystals of formula $[Ni(NO)(t\text{-}BuNC)_3]NO_3$, mp 85–88° (under nitrogen atmosphere). Treatment of the aqueous solution with an aqueous $NaBPh_4$ solution afforded an ionic complex $[Ni(NO)(t\text{-}BuNC)_3]BPh_4$, reddish violet needles, mp 112–113°. The ir spectrum (Nujol mull) resembles that of the parent nitrato complex except lacking the 1345- and 840-cm^{-1} bands characteristic of the NO_3 group.

Similarly, $Pd(O_2)(t\text{-}BuNC)_2$ was treated with nitric oxide in dichloromethane below −20°. The reaction mixture gradually turned into a light brown solution, and some decomposition of the dioxygen complex took place at ambient temperature. A yellow complex obtained in a trace amount showed ir absorption bands at 1320, 1275, and 1260 cm^{-1}, which are suggestive of the presence of either NO_2 or NO_3 group, but showed no ir band characteristic of a nitrosyl ligand. The insignificant yield as well as the instability in solution did not encourage further characterization.

(e) With Carbon Dioxide. A suspension of $Ni(O_2)(t\text{-}BuNC)_2$ in toluene was prepared by introducing oxygen into a solution of 0.223 g (0.57 mmol) of $Ni(t\text{-}BuNC)_4$ in 20 ml of toluene at −30°. Gaseous carbon dioxide was bubbled into the suspension at −20° for 2 hr. The initially pale green color changed into brown. After filtration the solvent was removed at ambient temperature *in vacuo* to leave residue from which was isolated, by treating with *n*-hexane, a brown hygroscopic carbonato complex of formula $Ni(CO_3)(t\text{-}BuNC)_2H_2O$, mp 130° dec, in 60% yield. From the above toluene distillate *t*-BuNCO was detected as $(t\text{-}BuNH)_2CO$ (0.62 mol/mol of $Ni(O_2)(t\text{-}BuNC)_2$).

Similarly, $Pd(O_2)(t\text{-}BuNC)_2$ was treated with carbon dioxide in toluene from −20° to ambient temperature to find no identifiable product. Alternatively, the reaction was carried out in dichloromethane at −70° in the presence of 2 mmol of *t*-BuNC and an excess of CO_2. The reaction mixture turned into yellow solution from which was isolated with *n*-hexane a small amount of yellow precipitate. The purification was attempted without success. The crude product showed no ir bands in the 1680-, 1260-, and 990-cm^{-1} regions characteristic of the carbonato stretchings.

(f) With Sulfur Dioxide. Gaseous sulfur dioxide was introduced under stirring into a suspension of 0.128 g (0.50 mmol) of $Ni(O_2)(t\text{-}BuNC)_2$ in 10 ml of *n*-hexane at −20°. The originally green color immediately turned into dark brown. When a large excess of SO_2 was added a dark brown liquid layer appeared under the colorless *n*-hexane layer. The excess SO_2 being evaporated off, the residue was chilled to afford, after washing with *n*-hexane and drying *in vacuo*, a very hygroscopic pale brown crystalline complex of $Ni(SO_4)(t\text{-}BuNC)_2$, mp 110–112° dec, in quantitative yield. The anhydrous sulfato complex is insoluble in most organic solvents except dichloromethane and chloroform. Upon contact with moist air it turned into a yellow hydrate, $Ni(t\text{-}BuNC)_2SO_4(H_2O)_n$. The magnetic susceptibility was measured by an automatic recording Faraday balance originally designed by Professor Kotani's group in this faculty.[49] The Curie-Weiss law was obeyed for a temperature range of 77–300°K with the magnetic moment of 0.93 BM and a Weiss constant of +0.06°.

Similarly, a suspension of 0.272 g (1 mmol) of $Pd(O_2)(t\text{-}BuNC)_2$ in *n*-hexane was treated with sulfur dioxide at −10° affording a brown

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(43) (a) R. F. Bader, *Mol. Phys.*, **3**, 137 (1960); (b) *Can. J. Chem.*, 40, 1164 (1962).

(44) L. Salem, *J. Chem. Phys.*, **38**, 1227 (1963); *Chem. Phys. Lett.*, 3, 99 (1969).

(45) L. Salem and J. S. Wright, *J. Amer. Chem. Soc.*, **91**, 5947 (1969).

(46) R. G. Pearson, *Theor. Chim. Acta*, **16**, 107 (1970).

(47) For a simplified isosceles system MO_2 (C_{2v}) the molecular orbital for the ground state may be assumed to be described as—$(a_1)^2(b_2)^2(b_1)^2$, A_1. Two lower excited states would then arise; *i.e.*, $(a_1)^2(b_2)^1(b_1)^2(a_2)^1$, B_1, and $(a_1)^1(b_2)^2(b_1)^2(a_2)^1$, A_2. The symmetry B_1 is relevant giving a direct product B_1 as the symmetry of the transition density.

(48) H. J. Dauben, Jr., L. R. Honnen, and K. M. Harmon, *J. Org. Chem.*, **25**, 1442 (1960).

(49) N. Nakano, J. Otsuka, and A. Tasaki, *Biochim. Biophys. Acta*, **236**, 222 (1971); M. Kotani, *et al.*, *ibid.*, **140**, 284 (1967).

mixture from which was isolated pale brown, hygroscopic crystals of formula $\mathrm{Pd(SO_4)}(t\text{-BuNC})_2$, mp 93–94° dec, in quantitative yield.

(g) With Benzoyl Halides. To a dichloromethane solution (20 ml) of 0.266 g (1.03 mmol) of $\mathrm{Ni(O_2)}(t\text{-BuNC})_2$ was added a solution of benzoyl bromide (0.383 g, 2.06 mmol) in dichloromethane (1 ml) slowly at −70° under stirring. The initially green color of the dioxygen complex immediately turned to reddish brown. After the reaction mixture was stirred for 5 hr at −70°, it was allowed to stand overnight in a refrigerator. The reaction mixture gave, upon vacuum distillation, 0.11 mmol of *t*-BuNCO (identified and weighed as $(t\text{-BuNH})_2\mathrm{CO}$) and a residue from which was isolated with ether extraction 0.261 g (0.68 mmol, 65.8%) of $\mathrm{NiBr_2}(t\text{-BuNC})_2$, mp 126°, as red needles. In addition to the nickel(II) complex, the ether extract afforded, upon treatment with *n*-hexane, 0.136 g (0.56 mmol, 54.6%) of dibenzoyl peroxide, mp 107–108°. Similarly, a suspension of 0.331 g (1.28 mmol) of $\mathrm{Ni(O_2)}(t\text{-BuNC})_2$ in toluene (20 ml) was treated with benzoyl chloride (0.4 ml, 3.43 mmol) at −10° to give 0.069 g (0.28 mmol, 23%) of dibenzoyl peroxide and *t*-BuNCO (2.0 mmol) together with an intractable brown material containing halogens.

(h) With Triphenylmethyl Tetrafluoroborate. To a dichloromethane solution (20 ml) of $\mathrm{Ni(O_2)}(t\text{-BuNC})_2$ (0.266 g, 1.03 mmol) was added solid triphenylmethyl tetrafluoroborate (0.68 g, 2.06 mmol) at −70° under stirring. After the reaction mixture was stirred for 5 hr at −70°, it was allowed to stand overnight in a refrigerator resulting in an orange yellow solution containing a small amount of white precipitates. The solution was distilled *in vacuo* at room temperature to give 0.003 g (0.02 mmol) of *t*-BuNCO and a residue which was extracted with carbon disulfide to isolate 0.270 g (0.68 mmol, 65.8%) of bis(triphenylmethyl) peroxide, white crystals, mp 185° (lit.[50] 185–186°). From the above residue was recovered with dichloromethane unreacted triphenylmethyl tetrafluoroborate (0.229 g, 33.7%). A dichloromethane-insoluble part of the residue showed ir bands at 2270 (ν_{NC}) and 837, 723 cm^{-1} (ν_{BF}) suggesting the presence of an isocyanide complex of Ni(II). However, the insolubility prevented further purification and characterization. Triphenylmethyl tetrafluoroborate does not react with gaseous dioxygen under these conditions.

(i) With Triphenylmethyl Bromide. To a dichloromethane solution (30 ml) of $\mathrm{Ni(O_2)}(t\text{-BuNC})_2$ (0.494 g, 1.93 mmol) was added solid triphenylmethyl bromide (1.329 g, 4.11 mmol) at −78° under stirring. The initial green color turned into wine red at −78°. After the reaction mixture was stirred for 5 hr at −78°, it was allowed to stand overnight in a refrigerator. The reaction mixture containing an appreciable amount of white powdery precipitates was distilled *in vacuo* at room temperature to give 0.1 mmol of *t*-BuNCO and red residue. The residue was extracted with diethyl ether to give 0.692 g (1.80 mmol, 93.5%) of $\mathrm{NiBr_2}(t\text{-BuNC})_2$, red needles, mp 125–126°, and the white fine powdery solid which was identified after recrystallization from $\mathrm{CS_2}$ as bis(triphenylmethyl) peroxide by its melting point and ir spectrum. The yield of this peroxide was 0.863 g (1.66 mmol, 86.4%).

II. Preparation of Some Nickel and Palladium Isocyanide Complexes. (a) $\mathrm{Ni(SO_2)}(t\text{-BuNC})_3$. To a suspension of 176 mg of $\mathrm{Ni}(t\text{-BuNC})_4$ in 10 ml of *n*-hexane was added an excess of gaseous $\mathrm{SO_2}$ at −20–0°. Deep red precipitates appeared instantly (when a large excess of $\mathrm{SO_2}$ was introduced the precipitates were dissolved resulting in a reddish purple solution). The excess of $\mathrm{SO_2}$ being allowed to evaporate off, the precipitates were collected under dry nitrogen atmosphere on a sintered filter, washed with dry *n*-hexane, and dried *in vacuo*. The yield was almost quantitative. The dark red precipitates were recrystallized from ether to give an analytical sample, mp 138–140° dec, mol wt (cryoscopic in benzene), 305 (calcd for monomer, 372). This complex is thermally fairly stable but sensitive to air. Upon exposure to moist air the intense color fades into orange yellow indicating oxidation to the sulfato complex (see below).

(b) "$\mathrm{Pd(SO_2)}(t\text{-BuNC})_2$."[31a] To a suspension of $\mathrm{Pd}(t\text{-BuNC})_2$ (40.9 mg) in *n*-hexane (10 ml) was added an excess of gaseous $\mathrm{SO_2}$ at −50°. The mixture was allowed to warm, under stirring, to room temperature. The initially orange color of the suspension turned into brown and finally yellow. The precipitate isolated from the mixture was recrystallized from toluene and ether to give orange yellow cubic crystals, mp 175–180° dec (15 mg, *ca.* 32%), mol wt (cryoscopic in benzene), 682 (calcd for dimer, 673). They are not extremely air-sensitive.

(c) $\mathrm{Ni(C_6H_5NO_2)}(t\text{-BuNC})_2$. A mixture of $\mathrm{Ni}(t\text{-BuNC})_4$ (0.196 mg, 0.5 mmol) and nitrobenzene (0.2 ml, *ca.* 2 mmol) in 15 ml of *n*-hexane was stirred at room temperature overnight affording reddish brown precipitates, which were washed with *n*-hexane and dried, mp 117–120° dec. The product is insoluble in most organic solvents and does not sublime even under high vacuum.

III. Reaction of Some Isocyanide Complexes with Dioxygen. (a) Reaction of $\mathrm{Ni(SO_2)}(t\text{-BuNC})_3$. Dioxygen was slowly introduced into a toluene solution (20 ml) of 0.136 g (0.39 mmol) of $\mathrm{Ni(SO_2)}(t\text{-BuNC})_3$ at −60°. The red color immediately turned into yellow. The yellow solution, after standing overnight at −25°, was concentrated affording the pale brown $\mathrm{Ni(SO_4)}(t\text{-BuNC})_2$, mp 100–110°, in nearly quantitative yield. Alternatively, the reaction of $\mathrm{Ni(SO_2)}(t\text{-BuNC})_3$ with oxygen was carried out in diethyl ether at −70° to give the sulfato complex in quantitative yield and a trace amount of *t*-BuNCO.

(b) Reaction of "$\mathrm{Pd(SO_2)}(t\text{-BuNC})_2$." A toluene solution of $\mathrm{Pd(SO_2)}(t\text{-BuNC})_2$ was stirred under dioxygen atmosphere at room temperature overnight to find neither dioxygen absorption nor color change, the sulfur dioxide complex being recovered unchanged.

(c) Reaction of $\mathrm{Ni(C_6H_5NO)}(t\text{-BuNC})_2$.[23] Dioxygen was introduced into a suspension of 0.166 g (0.5 mmol) of $\mathrm{Ni(C_6H_5NO)}(t\text{-BuNC})_2$ in 20 ml of *n*-hexane or toluene solution at −10° for 3 hr to give a pale green mixture from which was isolated quantitatively the dioxygen complex $\mathrm{Ni(O_2)}(t\text{-BuNC})_2$. Nitrosobenzene was recovered from the above filtrate by distillation, but neither free nitrobenzene nor the nitrobenzene complex, $\mathrm{Ni(C_6H_5NO_2)}(t\text{-BuNC})_2$, was detected.

Acknowledgment. We are grateful to Mr. Yoshiro Yamamoto for experimental assistance. We also wish to express our appreciation to the Ministry of Education, Japanese Government, for financial support.

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(50) M. Gomberg, *Chem. Ber.*, **33**, 3150 (1900).