crystals, mp 208° dec, were isomorphous with an authentic sample of $IrH_2Cl(Ph_3P)_3$. *Anal.* Calcd for $C_{54}H_{47}ClP_3Ir$: C, 63.8; H, 4.7; Cl, 3.5. Found: C, 62.6; H, 5.2; Cl, 2.9.

(c) **Hydrogen.** There was no change in the infrared spectrum of the solution when hydrogen was passed at 25° (1 atm) through a solution of "$IrHCl(Ph_3P)_3$" (0.2 g) in 30 ml of benzene. Refluxing for 1 hr and slow addition of petroleum ether (bp 60–80°) gave colorless, light-sensitive crystals (0.17 g, 85%) isomorphous with $IrH_2Cl(Ph_3P)_3$. *Anal.* Found: C, 64.1; H, 4.6; Cl, 3.8.

(d) **Deuterium.** The reaction was carried out as under (c) to give a complex isomorphous with $IrH_2Cl(Ph_3P)_3$. From 0.25 g of "$IrHCl(Ph_3P)_3$" was obtained 0.14 g (70%) of $IrH(D)H(D)Cl(Ph_3P)_3$ (see text).

(e) **Hydrogen Chloride.** Dry hydrogen chloride was passed into a refluxing solution of "$IrHCl(Ph_3P)_3$" (0.3 g) in benzene (20 ml) for 30 min. The color changed from pale yellow to yellow. After 40 ml of petroleum ether (bp 80–100°) had been added, the solution was evaporated to ~30 ml at 15 mm; the solid was filtered off and recrystallized from benzene–petroleum ether (bp 60–80°) to give 0.22 g (71%) of pale yellow $IrHCl_2(Ph_3P)_3$. *Anal.* Calcd for $C_{54}H_{46}Cl_2P_3Ir$: C, 61.7; H, 4.4; Cl, 6.7. Found: C, 61.4; H, 4.6; Cl, 6.4.

(f) **Deuterium Chloride.** Reaction of DCl with 0.3 g of "$IrHCl(Ph_3P)_3$" as under (e) gave 0.19 g (62%) of $IrDCl_2(Ph_3P)_3$, isomorphous with $IrHCl_2(Ph_3P)_3$.

Kinetic Measurements. The rates of hydrogen abstraction for the phosphine complexes were measured by following the appearance of the band due to ν(Ir–H) at *ca.* 2200 cm^{-1}. Only one concentration of each complex was used (1.44×10^{-3} *M*), this being near the limit of solubility of the $(p\text{-}FC_6H_4)_3P$ complex. Lower concentrations would have made the initial stages of reaction difficult to follow. The complexes were dissolved in degassed benzene; the solution was placed in a 1-mm cell having sodium chloride windows and quickly transferred to the sample beam of the Perkin-Elmer 225 spectrophotometer. With a 1-mm cell containing pure benzene in the reference beam, the spectrum was scanned continuously between 2500 and 1800 cm^{-1}. The temperature in the sample beam was 39.5 ± 0.5°. The infinity reading was taken as six half-lives (some decomposition being evident thereafter), and the reproducibility was within experimental error.

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Oxygen Complexes of Nickel and Palladium. Formation, Structure, and Reactivities

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Abstract: Novel oxygen complexes of formula $M(O_2)(RNC)_2$ (R = *t*-butyl and cyclohexyl for M = Ni; R = *t*-butyl for M = Pd) were prepared by oxygenation of the corresponding zerovalent isocyanide complexes, $M(RNC)_4$ or $M(RNC)_2$. These diamagnetic, thermally relatively unstable oxygen complexes are intermediates in the catalytic oxygenation of alkyl isocyanides. They are insoluble in nonpolar solvents and not monomeric in the solid state. The ir, nmr, and electronic spectra and magnetic data were collected to deduce essentially square-planar structures with an intermolecular axial interaction through the O_2 ligand. The chemical behaviors toward reagents of varying donor–acceptor properties were studied to show that reagents of strong electron affinities release oxygen while electron donor reagents, *e.g.*, PR_3 and RNC, cause oxygen-atom transfer. The reaction of $Ni(O_2)(t\text{-}BuNC)_2$ with CH_3NC involves incipient formation of $Ni(O_2)(t\text{-}BuNC)_2(CH_3NC)_2$ and $Ni(O_2)(t\text{-}BuNC)(CH_3NC)_2$ prior to the oxygen-atom transfer. Ligation of RNCO to Ni(O) was confirmed by isolation of $Ni(RNCO)(RNC)_2$, a product of oxygen-atom transfer. The isocyanate ligand was shown to be quite susceptible to substitution with RNC as required for the catalytic oxygenation of RNC.

Recently it was found[1] that alkyl isocyanides can be catalytically oxygenated with molecular oxygen into the corresponding alkyl isocyanates in the presence of a low-valent nickel complex such as bis(1,5-cyclooctadiene)nickel or tetrakis(isocyanide)nickel. Eventually a peroxo complex, $Ni(O_2)(t\text{-}BuNC)_2$, was isolated as pale green crystals. Closely related peroxophosphine complexes, $M(O)_2(PPh_3)_2$(M = Ni, Pd, and Pt), have been reported[2,3] to be formed from $M(PPh_3)_{3\sim4}$ and an oxygen molecule. Analogous oxidative additions of ligands (L), *e.g.*, tetracyanoethylene, carbon disulfide, and others, to $M(PPh_3)_{3\sim4}$ giving $ML(PPh_3)_2$ have been extensively surveyed.[4–15] The per-

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oxophosphine complexes are effective for catalytic oxygenation of triarylphosphine to the phosphine oxide. These peroxo complexes may be regarded as a simplest oxygenase model since molecular oxygen is activated, through coordination to metal, to transfer an oxygen atom into the substrate; and in the presence of an excess substrate the metal species is apparently reverted to the active complex after the oxygenated product is released from the metal. RNC or PR_3 in these systems functions not only as a substrate but also as a "cofactor" (a ligand) maintaining an appropriate electronic structure of the metal species. Detailed studies on the chemical structures and properties are required to obtain insight into the mechanism of the catalytic oxygenation process. This paper will describe results of our studies on the preparative and structural chemistries of the peroxo isocyanide complexes of nickel and palladium. Also included are their behavior in substitution reactions of O_2 ligand and oxygen-atom transfer reactions.

Results and Discussion

Preparation. Successful preparations of the peroxo nickel or palladium complexes rely on particular aliphatic isocyanide complexes, $Ni(RNC)_4$, $Ni(RNC)_2$, and $Pd(RNC)_2$ where R is *t*-butyl or cyclohexyl for nickel and only *t*-butyl for palladium. Attempted preparations of peroxo complexes from other isocyanide compounds, *e.g.*, $Ni(ArNC)_4$ or $Pd(cyclo\text{-}C_6H_{11}NC)_2$, were unsuccessful.

The new isocyanide complexes $Ni(t\text{-}BuNC)_4$ and $Ni(t\text{-}BuNC)_2$ are best prepared by treatment with *t*-BuNC of bis(π-1,5-cyclooctadiene)nickel, $Ni(C_8H_{12})_2$. This method finds general applicability for the preparation of tetrakis isocyanide complexes of formula $Ni(RNC)_4$. When the stoichiometry, $t\text{-}BuNC/Ni(C_8H_{12})_2$, for the preparative reaction is restricted to 2, a dark reddish brown crystalline complex of composition $Ni(t\text{-}BuNC)_2$ is formed. The ir spectrum (Nujol mull) suggested a cluster structure having bridging isocyanide groups (see Experimental Section), but the molecular structure was left to be elucidated.

Introduction of pure gaseous oxygen or air into an ether, tetrahydrofuran, or aromatic hydrocarbon solution of $Ni(RNC)_4$ below −20° produces the pale green peroxo complex $Ni(O_2)(RNC)_2$ (R = *t*-butyl and cyclohexyl). The reaction of an oxygen molecule with "$Ni(t\text{-}BuNC)_2$" in ether solution takes place most readily below −20° affording the same peroxo complex almost quantitatively. Similarly the almost colorless peroxo palladium complex $Pd(O_2)(t\text{-}BuNC)_2$ was obtained from an ether or a tetrahydrofuran solution of $Pd(t\text{-}BuNC)_2$. It is to be noted that although these peroxo nickel complexes in solid state are fairly stable in air at room temperature, a dried sample in an amount of more than 0.5 g often explodes with or even without shock. They show instability in solution; decomposition of the palladium complex in $CHCl_3$ solution takes place rapidly at 0° while the nickel complexes in $CHCl_3$ decomposes slowly at that temperature. The instability prevented molecular weight measurement. $Pd(O_2)(t\text{-}BuNC)_2$ in crystalline state appears to be fairly stable at ambient temperature while $Ni(O_2)(t\text{-}BuNC)_2$ deteriorates slowly at that temperature. The presence of moisture accelerates the decomposition. From their electronic spectra which will be described later it seems reasonable that the palladium complex is thermally more stable than the corresponding nickel complex.

Structure. The nmr spectrum of $Ni(O_2)(t\text{-}BuNC)_2$ was measured in chloroform, benzotrifluoride, and perdeuteriotoluene at −20° and showed only one singlet resonance for the *t*-butyl protons (Table I). The chemical shift is very much solvent dependent, but does not depart from a range for diamagnetic isocyanide complexes. Consistently, the magnetic susceptibility of $Ni(O_2)(t\text{-}BuNC)_2$ in the solid state was measured by the usual Faraday method and only a feeble magnetic moment (0.13 BM) was found, indicating temperature-independent paramagnetism.

The infrared spectrum of peroxo nickel complexes shows a moderately intense band (900–800-cm^{-1} region). This has been assigned as the "O–O stretching band" from the isotopic study;[16] upon isotopic substitution with a mixture of $^{16}O_2$, $^{16}O\text{–}^{18}O$, and $^{18}O_2$ (58.3, 32.4, and 9.3 mol%), $Ni(O_2)(t\text{-}BuNC)_2$ shows three bands at 898, 873, and 848 cm^{-1}. The 898-cm^{-1} band is the one observed in $Ni(O_2)(t\text{-}BuNC)_2$ which has been prepared with ordinary oxygen. The splitting is in good agreement with the calculated wave numbers, 898, 873, and 846 cm^{-1}, based on the free diatomic molecule. Thus linear coordination of an oxygen molecule (M–O–O) may be excluded. The side-on coordination forming an isosceles triangle with the metal has been established for Vaska's oxygen complex, $IrCl(O_2)(CO)(PPh_3)_2$,[17,18] which also shows three isotopic bands at 856, 832, and 809 cm^{-1}.[19,20] The peroxo palladium complex shows the three isotopic bands at 893, 868, and 837 cm^{-1} indicating similar geometry for O_2 coordination.[16]

The NC stretching absorptions of these peroxo complexes occur at the 2200–2170-cm^{-1} region as two intense bands. Table II summarizes the NC stretching frequencies of the peroxo and related nickel and palladium complexes. Observation of the two NC stretching bands of equal intensity implies *cis* ligation of the isocyanides (a local symmetry C_{2v}) whereas one strong band for $NiI_2(t\text{-}BuNC)_2$ is indicative of the *trans* configuration. In view of the high NC stretching frequencies,

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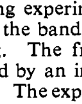


for a number of O_2 complexes, *e.g.*, $Ni(O_2)(t\text{-}BuNC)_2$ and $RhX(O_2)(L)_2(CNR)$($L = PPh_3$, $AsPh_3$), using experimental data obtained by use of $^{18}O_2$. The result indicates that the band at 860–900 cm^{-1} is not solely due to "pure" O–O stretching. The frequency of "so-called" O–O stretching (A_1 mode) is increased by an increase of the M–O symmetry stretching frequency (A_1 mode). The experimentally observed constancy of the "O–O stretching" could be a consequence of two opposing factors; *viz.* an increase of O–O force constant in most cases reduces the M–O_2 force constant. (b) These bands have already been thought not to be "pure" O–O stretching: J. A. McGinnety, J. A. Ibers, and R. J. Doedens, *Science*, **155**, 709 (1967).

Table I. Nmr Spectra[a] of the Peroxo and Related Compounds

Compounds[d]	Solvent $CHCl_3$	 $C_6H_5CF_3$	 $C_6D_5CD_3$
Ni(t-BuNC)$_4$	8.59	8.89	8.97
$Ni(O_2)$(t-BuNC)$_2$	8.53	9.02	9.23[c]
NiI_2(t-BuNC)$_2$	8.52	8.95	9.38
$Pd(O_2)$(t-BuNC)$_2$	8.51[b]		
PdI_2(t-BuNC)$_2$	8.46		
t-BuNC	8.53	8.81	9.00

[a] Measured at −20°, unless otherwise specified, using TMS as internal reference. [b] Measured at −30°. [c] Measured in a very dilute solution because of the poor solubility. [d] The observed resonance for all these complexes is a singlet, but the one for free *t*-BuNC is a triplet (see Table IV).

Table II. Infrared Isocyanide Stretching Absorptions of Peroxo and Related Complexes of Nickel and Palladium[a]

	ν_{NC}, cm^{-1}	Intensity	Other bands, cm^{-1}
Ni(t-BuNC)$_4$	2000	vs	1205(δC–(CH$_3$)$_3$)
$Ni(O_2)$(t-BuNC)$_2$	2196	s	1203(δC–(CH$_3$)$_3$)
	2178	s	898(νO–O)
$Ni(O_2)$(cyclo-$C_6H_{11}NC)_2$	2204	s	904(νO–O)
	2174	s	
Ni(TCNE)(t-BuNC)$_2$	2194	s	2219 (νCN)
	2179	s	2220
			1195 (δC–(CH$_3$)$_3$)
			1203
NiI_2(t-BuNC)$_2$	2194	s	1197(δC–(CH$_3$)$_3$)
Pd(t-BuNC)$_2$	2108	s	1700(ν bridge NC)
			1200(δC–(CH$_3$)$_3$)
$Pd(O_2)$(t-BuNC)$_2$	2207	s	1200(δC–(CH$_3$)$_3$)
	2190	s	893(νO–O)
Pd(TCNE)(t-BuNC)$_2$	2220	s	1198(δC–(CH$_3$)$_3$)
	2210		
PdI_2(t-BuNC)$_2$	2215	s	1198(δC–(CH$_3$)$_3$)

[a] Measured in Nujol mull.

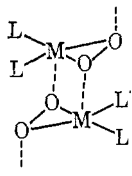
Table III. Electronic Spectra

	Absorption maxima, mμ	Intensity, ϵ
$Ni(O_2)$(t-BuNC)$_2$	380[a]	316[a]
	600[a]	38[a]
	400[b]	
	680[b]	
$Pd(O_2)$(t-BuNC)$_2$	600[b]	

[a] In $CHCl_3$ solution at −30°. [b] Solid state (reflectance).

which are comparable to those of Ni(TCNE)(*t*-BuNC)$_2$ (TCNE = tetracyanoethylene) and NiI_2(*t*-BuNC)$_2$, electrons derived from the originally zerovalent metal are considered to be delocalized on the metal–oxygen bond and the degree of electron transfer to the O_2 ligand is such that the apparent (formal) oxidation state of the metal is near that of the divalent state.[21] From the π-accepting ability of oxygen and isocyanide ligands, a square-planar structure may be suggested. However, a discrete square-planar structure is unlikely for $Ni(O_2)$(*t*-BuNC)$_2$ in the solid state as indicated from the poor solubilities in many organic media except organic halides like dichloromethane and chlorobenzene or strong donor solvents such as pyridine or alkyl isocyanide.

Table III summarizes the electronic spectra of these peroxo complexes in chloroform solution and in the solid state. In addition to a charge transfer band at 380 mμ a weak d–d band was observed at 600 mμ in solution or at 680 mμ in the solid state for the peroxo nickel complex. A similar weak band was also observed for the analogous peroxo Pd complex at 600 mμ in the solid state. Attempts to obtain a solution spectrum of the palladium complex were unsuccessful due to the instability of the palladium complex in solution even at −30°. Accepting the apparent oxidation state of Ni(II), the band at 600 mμ is incompatible with the square-planar structure. A tetrahedral structure can be excluded on the basis of the strong ligand field expected for isocyanide; a distorted octahedral structure with two long axial bonds is left to be considered. The transition, $^3A_2$ to $^3T_1$, for a regular octahedral d^8 complex generally constitutes the longest wavelength absorption in the visible region. The observed d–d band may correspond to a transition from $^3A_2$ to either $^3T_2$ ($^3A_1$, $^3B_1$, and $^3B_2$ for C_{2v}) or $^3T_1$ ($^3A_2$, $^3B_1$, and $^3B_2$ for C_{2v}). Axial interactions between square-planar molecules forming a macromolecule where each metal ion assumes an octahedron are found in xanthate, dithiocarbamate, and like complexes of Ni(II).[22] The difference in maxima between the absorption and reflectance spectrum is then intelligible in terms of the axial interaction. The provisional, idealized structure is depicted below. Dissolution in a donor solvent will destroy the oxygen bridging resulting in monomeric penta- (*i.e.*, $Ni(O_2)$(*t*-BuNC)$_2$L) or hexacoordinate compounds (*i.e.*, $Ni(O_2)$(*t*-BuNC)$_2$L$_2$); see eq 2 in Reactions. The apparent hexacoordination in the solid state may require comments since only a few octahedral Ni(II) complexes are known to be diamagnetic.[22b] The absence of usual paramagnetism is in accord with a picture where the ligands in the plane exert fairly strong fields. The assumed coplanarity of O_2 and two isocyanide ligands finds support in the structure of an analogous oxygen complex, $Pt(O_2)(PPh_3)_2$, in which the similar coplanarity was recently demonstrated by X-ray analysis.[23]



M = Ni, Pd
L = *t*-BuNC

Accepting this stereochemistry one can find a rationalization for the observed trends in the physical characteristics of the nickel and palladium complexes such as their thermal stabilities and the NC stretching frequencies. Thus in accord with the relative thermal stabilities the ligand splitting is larger in the palladium complex than in the nickel congener (Table III). Further, consistent with the higher ionization potential of

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[21] The degree of electron transfer cannot be measured with certainty. Such ambiguity between the concept of formal oxidation state and actual valency state indicates that an ionic model and the valence bond term do not provide an adequate model for such transition metal complexes.

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$Pd(O)$, the NC stretching frequencies for Pd complexes are generally higher than for the Ni analogs (Table II). Among the Pd complexes, the NC stretching frequency of $Pd(O_2)(t\text{-}BuNC)_2$ is slightly lower than that of $Pd(TCNE)(t\text{-}BuNC)_2$ or $PdI_2(t\text{-}BuNC)_2$ implying less electron transfer to the O_2 ligand. A question then arises as to the relative bond strengths of metal–oxygen in $M(O_2)(t\text{-}BuNC)_2$; M = Ni, Pd. This will be discussed separately. Suffice it to note that our calculation of the force constants f_{M-O} for $Ni(O_2)(t\text{-}BuNC)_2$ and $Pd(O_2)(t\text{-}BuNC)_2$ shows a lower value for the latter complex. The trend appears to agree with the enhanced instability in solution (*vide supra*) as well as with the greater activity in catalytic oxygenation reactions of the palladium complex, although the correlation between the force constants and bond energies has not been established.

Reactions. Reactions of $Pt(O_2)(PPh_3)_2$ with various reagents such as CO_2, SO_2, NO, NO_2, etc., have been examined by several authors.[5,24] However, only a few reports have been made on the nickel[3] or palladium congener. Our primary interest in the reactivity concerns the chemical behavior of the peroxo ligand in $Ni(O_2)(RNC)_2$. Through this study we hope to gain knowledge of the nature of oxygen to metal bonding and also to shed some light on the mechanism of the oxygen-atom transfer reactions relating to catalytic oxidations.

Firstly, the irreversibility of oxygen coordination was established; solid $Ni(O_2)(t\text{-}BuNC)_2$ was heated near 60° *in vacuo* (10^{-4} mm) and no appreciable decomposition was found. The complex suspended in toluene was stirred at ambient temperature to afford 1 mol of t-BuNCO and a brown cluster complex of unknown structure from which was obtained the known $Ni(t\text{-}BuNC)_4$ by treating with an excess of t-BuNC (eq 1). Compared to the metal–oxygen bonding in $IrCl(O_2)(CO)(PPh_3)_2$, whose reversibility is well known, an enhanced electron transfer to the O_2 ligand is apparent in $Ni(O_2)(RNC)_2$.

(1)

When an electron-donor ligand approaches the coordination sphere by breaking the relatively weak axial coordination bond, further electron transfer to the O_2 ligand may take place. Then the electron drainage into an antibonding π orbital of the coordinated O_2 will facilitate O–O bond cleavage giving rise to transfer of an O atom to a ligand. An attempted isolation of a discrete molecule of formula $Ni(O_2)(t\text{-}BuNC)_2(L)$ (L = RNC or PPh_3) was not successful due to the ready transfer of an oxygen atom to the isocyanide ligand (*vide infra*). However, an apparent pentacoordination can be realized in a tetracyanoethylene (TCNE) complex; $Ni(TCNE)(t\text{-}BuNC)_3$ was found stable enough to be isolated. This is important because the oxidation states of nickel in $Ni(O_2)(t\text{-}BuNC)_2$ and $Ni(TCNE)(t\text{-}BuNC)_2$ would not differ much as deduced from their NC stretching frequencies (Table II). Further, an indication for ligation of 2 mol of CH_3NC to $Ni(O_2)(t\text{-}BuNC)_2$ was obtained in the cold chloroform solution by means of nmr spectroscopy. Due to coupling with the nuclear magnetic moment of nitrogen atom ($I = 1$), free methyl or t-butyl isocyanide shows a triplet resonance with a small coupling constant for the protons. Upon coordination to a metal the triplet converges to a singlet owing to the quadrupole relaxation; the phenomena appear to be quite common to a variety of metal centers, *e.g.*, Cu(I), Ag(I), Ni(II), Ni(O), Pd(II), Pd(O), Rh(I), etc.[25] As shown in Table IV, a mixture of $Ni(O_2)(t\text{-}BuNC)_2$ and 2 mol of CH_3NC in $CHCl_3$ at −19° showed two resonances at τ 6.77 and 8.55 assignable, respectively, to the coordinated CH_3NC and $(CH_3)_3CNC$ protons on the basis of the absence of magnetic coupling. When the temperature was raised to 3°, the resonance of t-butyl protons at τ 8.55 restored the coupling, indicating onset of dissociation of t-BuNC ligands (eq 2).

Table IV. Nmr Studies[a] of Ligation of CH_3NC to $Ni(O_2)(t\text{-}BuNC)_2$

System	Chemical shift, τ	Splitting[b]
Free CH_3NC	6.85	t (J = 1.6 Hz)
Free t-BuNC	8.53	t (J = 2.0 Hz)
$2CH_3NC + Ni(O_2)(t\text{-}BuNC)_2$	6.77	s
	8.55	s
$2CH_3NC + Ni(O_2)(t\text{-}BuNC)_2$[c]	6.77	s
	8.55	t (J = 2.0 Hz)

[a] Measured in chloroform at −19°; internal reference, TMS. [b] t = triplet, s = singlet. [c] At 3°.

$$Ni(O_2)(t\text{-}BuNC)_2 + 2CH_3NC \overset{-19°}{\rightleftharpoons} Ni(O_2)(t\text{-}BuNC)_2(CH_3NC)_2 \overset{+3°}{\rightleftharpoons} Ni(O_2)(t\text{-}BuNC)(CH_3NC)_2 + t\text{-}BuNC \quad (2)$$

The oxygen-atom transfer to isocyanide ligands, which is not appreciable near 0°, begins about 30°. Thus, from the reaction of $Ni(O_2)(t\text{-}BuNC)_2$ with an excess of t-BuNC in toluene at ambient temperature were isolated nearly 2 mol of t-BuNCO and some $Ni(t\text{-}BuNC)_4$ (eq 3). When $Ni(O_2)(t\text{-}BuNC)_2$ was treated with an excess of PPh_3 at ambient temperature, the oxygen atoms were exclusively transferred to the phosphine affording Ph_3PO and $Ni(t\text{-}BuNC)_2(PPh_3)_2$ (eq 4). The phosphine oxide may be derived from an incipient species $Ni(O_2)(PPh_3)_2$ which is unstable[3] compared to the corresponding isocyanide complex. Consistent with this is the catalytic oxygenation rate observed with a nickel catalyst, which is faster for PPh_3 than for t-BuNC, as will be described separately.[26] The reaction of CH_3NC (or cyclo-$C_6H_{11}NC$) with $Ni(O_2)(t\text{-}BuNC)_2$ produced a mixture of t-BuNCO and CH_3NCO (or cyclo-$C_6H_{11}NCO$). In view of equilibrium 2 several mixed isocyanide complexes may be involved prior to the oxygen transfer. Once isocyanate is formed in the coordination sphere,

$$Ni(O_2)(t\text{-}BuNC)_2 + 4t\text{-}BuNC \longrightarrow Ni(t\text{-}BuNC)_4 + 2t\text{-}BuNCO \quad (3)$$

$$Ni(O_2)(t\text{-}BuNC)_2 + 4PPh_3 \longrightarrow Ni(t\text{-}BuNC)_2(PPh_3)_2 + 2Ph_3PO \quad (4)$$

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[24] (a) C. D. Cook and G. S. Jauhal, *J. Amer. Chem. Soc.*, **89**, 3066 (1967); (b) J. P. Collman, M. Kubota, and W. Hosking, *ibid.*, **89**, 4809 (1967); (c) J. P. Collman, *Accounts Chem. Res.*, **1**, 136 (1968); (d) R.Ugo, F. Conti, S. Cenini, R. Mason, and G. B. Robertson, *Chem. Commun.*, 1498 (1968).

[25] S. Otsuka, unpublished data.

[26] S. Otsuka, *et al.*, submitted for publication.

it will readily be replaced by isocyanides or other donor reagents available in the system to yield $\mathrm{Ni(RNC)_4}$ or $\mathrm{Ni(RNC)_2L_2}$ (*e.g.*, L = $\mathrm{PPh_3}$). In the absence of these donor reagents the main nickel species is a cluster complex containing the isocyanate as described above (*cf.* eq 1).

A very unstable isocyanate nickel complex of formula $\mathrm{Ni(}t\mathrm{\text{-}BuNCO)(}t\mathrm{\text{-}BuNC)_2}$ was isolated at low temperature from a reaction mixture involving "$\mathrm{Ni(}t\mathrm{\text{-}BuNC)_2}$" and *t*-BuNCO but the instability prevented characterization. The lability of the isocyanate ligation appears to be a requirement for a successful catalytic oxidation of isocyanide.

$$\mathrm{Ni(}t\text{-}\mathrm{BuNC)_2} + t\text{-}\mathrm{BuNCO} \rightleftharpoons \mathrm{Ni(}t\text{-}\mathrm{BuNCO)(}t\text{-}\mathrm{BuNC)_2} \xrightleftharpoons{2t\text{-}\mathrm{BuNC}} \mathrm{Ni(}t\text{-}\mathrm{BuNC)_4} + t\text{-}\mathrm{BuNCO} \quad (5)$$

Ligation of an electron donor leading to such a species as $\mathrm{Ni(O_2)(RNC)_2L}$ will certainly enhance the electron transfer to the π_g orbitals of $\mathrm{O_2}$ ligand, leading to O–O bond cleavage or oxygen-atom transfer to ligands. It will then be of interest to examine reactions with strong electron accepting substances where competition for the dπ electrons may occur between the oxygen ligand and the attacking reagent. Treatment of $\mathrm{Ni(O_2)(}t\text{-}\mathrm{BuNC)_2}$ with a slight excess of TCNE gave rise to a complex, $\mathrm{Ni(TCNE)(}t\text{-}\mathrm{BuNC)_2}$, releasing molecular oxygen together with a small amount of *t*-BuNCO. Thus it appears that dπ–pπ type bonding contributes to a great extent to the metal–oxygen bond and that an effective reduction in electron density in the metal center leads to the metal–oxygen bond cleavage. Oxidation of $\mathrm{Ni(O_2)(}t\text{-}\mathrm{BuNC)_2}$ with 1 mol of iodine or bromine producing a quantitative amount of oxygen is understood as a complete reverse flow of electrons from the oxygen ligand to halogens. $\mathrm{BF_3 \cdot Et_2O}$ reacts with the complex in a similar way releasing oxygen molecule.

Weaker dπ acceptors, *e.g.*, olefins or aromatic hydrocarbons, do not accept the oxygen-atom transfer and are left unoxidized, while the peroxo complex decomposes thermally producing the isocyanate (*cf.* eq 1). The above olefins and aromatics include typical acceptors for singlet oxygen,[27] *i.e.*, 1,3-cyclohexadiene, tetramethylethylene, or anthracene. Thus far we are unable to find any reaction characteristic of the $^1\Delta_g$ state.

Some bonding theories have already been propounded for the metal–oxygen bonding in the well-known oxygen complexes of Ir and Pt,[28,29a,b] and attempts were made to describe the electronic structure of coordinated oxygen[29c] or related molecules such as acetylene[29b,d] in terms of the excited-state configurations. Further studies on the reactivity of $\mathrm{M(O_2)(RNC)_2}$ to give insight into the electronic structure are now in progress.

Experimental Section

Physical Measurements. Ir spectra of Nujol-mulled samples were recorded on a Hitachi-Perkin-Elmer Model 225, nmr spectra of solution samples were recorded on a 100-Mc instrument of Jeol JNM 4H-100 Model, and electronic spectra of absorption and diffuse reflectance were recorded on a Cary 15 and a Shimadzu MPS-50L. All preparations and physical measurements for solutions of peroxo nickel complexes were performed below −15° to prevent decomposition. The extreme instability of peroxo palladium complexes in solution prevented detailed studies on their solution chemistry. Magnetic susceptibility was measured by a Faraday balance at 77 and 298 °K.

Materials. The following compounds were prepared according to known methods; *t*-butyl isocyanide,[30] methyl isocyanide,[31] cyclohexyl isocyanide,[32] bis(1,5-cyclooctadiene)nickel,[33] and π-cyclopentadienyl-π-allylpalladium.[34] All chemicals commercially available were of reagent grade.

I. **Isocyanide Complexes.** $\mathbf{Ni(}\boldsymbol{t}\mathbf{\text{-}BuNC)_4}$ was prepared by treating 0.776 g (2.82 mmol) of $\mathrm{Ni(C_8H_{12})_2}$ suspended in 15 ml of *n*-hexane with 2.34 g (3 ml, 28.2 mmol) of *t*-BuNC. Pale yellow precipitates in the solution were filtered, washed with *n*-hexane, and recrystallized from a mixture of ether and ethanol to give pale yellow crystals, 1.0 g (91% yield), mp 170° dec.

Anal. Calcd for $\mathrm{C_{20}H_{36}N_4Ni}$: C, 61.43; H, 9.21. Found: C, 61.16; H, 9.42.

"$\mathbf{Ni(}\boldsymbol{t}\mathbf{\text{-}BuNC)_2}$" was prepared according to the known method[35] from $\mathrm{Ni(C_8H_{12})_2}$. The reddish brown microcrystalline complex was washed with *n*-hexane and recrystallized from ether at −78°. The extremely air-sensitive complex was characterized by its ir spectrum which shows bands at 2020 (s, broad), 1605 (m), and 1210 (m) and in benzene at 2020 (s), 1603 (m), and 1210 cm^{-1} (m). The 2020- and 1603-cm^{-1} bands are assignable to the terminal and bridging isocyanide groups, respectively. Its nmr spectrum in benzene showing three singlet signals of approximately equal intensity at 1.83, 1.19, and 1.06 ppm from TMS is also characteristic of this polynuclear complex.

$\mathbf{Ni(cyclo\text{-}C_6H_{11}NC)_4}$ was prepared similarly from $\mathrm{Ni(C_8H_{12})_2}$. Recrystallization from *n*-hexane gave pale yellow crystals, mp 75° dec.

Anal. Calcd for $\mathrm{C_{28}H_{44}N_4Ni}$: C, 67.92; H, 8.89; N, 11.32. Found: C, 67.93; H, 8.98; N, 11.05.

$\mathbf{Pd(}\boldsymbol{t}\mathbf{\text{-}BuNC)_2}$ was prepared following the procedure for preparation of $\mathrm{Pd(}i\text{-}\mathrm{C_3H_7NC)_2}$ or $\mathrm{Pd(cyclo\text{-}C_6H_{11}NC)_2}$.[36] Thus, 0.213 g (1 mmol) of Pd $\mathrm{(C_3H_5)(C_5H_5)}$ dissolved in 25 ml of pentane was treated with 0.332 g (0.425 ml, 4 mmol) of *t*-BuNC at −10–5°. The solid product was washed with pentane to give 0.15 g (55% yield) of orange needles, mp 130° dec. The complex is very soluble in benzene and toluene, soluble in ether, and insoluble in hexane. Like $\mathrm{Ni(}t\text{-}\mathrm{BuNC)_2}$, dissolution of $\mathrm{Pd(}t\text{-}\mathrm{BuNC)_2}$ into $\mathrm{CHCl_3}$ results in its oxidative decomposition.

Anal. Calcd for $\mathrm{C_{10}H_{18}N_2Pd}$: C, 44.05; H, 6.61; N, 10.28. Found: C, 43.67; H, 6.61; N, 10.25.

The ir spectrum (Nujol mull) showed bands at 2108, 1780, and 1200 cm^{-1}. The nmr spectrum of a benzene solution showed a singlet signal at 1.29 ppm (from TMS) for the *t*-butyl protons.

$\mathbf{NiI_2(}\boldsymbol{t}\mathbf{\text{-}BuNC)_2}$ was prepared from 1.24 g (4 mmol) of anhydrous $\mathrm{NiI_2}$ suspended in 50 ml of tetrahydrofuran by adding 2.34 g (3 ml, 28.2 mmol) of *t*-BuNC at 20° and stirring for 3 hr at this temperature. The solvent was removed *in vacuo* to leave residues which were extracted with *n*-hexane. By chilling the extract at −30° deep brown needles, mp 135°, were obtained in quantitative yield. This is the first reported successful isolation of an isocyanide complex of divalent nickel halide.

Anal. Calcd for $\mathrm{C_{10}H_{18}N_2I_2Ni}$: C, 25.27; H, 3.80; N, 5.97. Found: C, 25.62; H, 3.76; N, 5.85.

$\mathbf{PdI_2(}\boldsymbol{t}\mathbf{\text{-}BuNC)_2}$ was prepared by treating 0.80 g (2 mmol) of $\mathrm{PdI_2}$ suspended in 10 ml of benzene with 2.34 g (3 ml, 28.2 mmol) of *t*-BuNC. Concentration followed by addition of cold *n*-hexane produced orange-red needles, mp 166°, in quantitative yield.

Anal. Calcd for $\mathrm{C_{10}H_{18}N_2I_2Pd}$: C, 22.80; H, 3.42; N, 5.32. Found: C, 23.14; H, 3.42; N, 5.34.

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Ni(TCNE)(*t*-BuNC)$_2$ was obtained by treating 0.225 g (1 mmole) of Ni(*t*-BuNC)$_2$ in 20 ml of toluene with 0.512 g (4 mmol) of TCNE at room temperature for 3 hr. Upon cooling deep brown crystals were precipitated. Recrystallization from toluene gave 0.282 g (80%) of the complex, mp 160–165° dec.

Anal. Calcd for $C_{16}H_{18}N_6Ni$: C, 54.43; H, 5.13; N, 23.79. Found: C, 55.04; H, 5.68; N, 23.26.

Pd(TCNE)(*t*-BuNC)$_2$ was obtained by treating 0.245 g (1 mmol) of Pd(*t*-BuNC)$_2$ in 20 ml of toluene with 0.512 g (4 mmol) of TCNE at −20–0° for 5 hr. Dark yellow crystals were recrystallized from toluene to give 0.30 g (75%) of the complex, mp 145° dec.

Anal. Calcd for $C_{16}H_{18}N_6Pd$: C, 47.95; H, 4.50; N, 20.98. Found: C, 48.13; H, 4.42; N, 20.54.

II. **Peroxo Complexes.** Ni(O$_2$)(*t*-BuNC)$_2$ was prepared by introduction of dry oxygen at −20° into an ether or tetrahydrofuran solution (15 ml) of 0.2 g of Ni(*t*-BuNC)$_4$. Rapid O$_2$ absorption was accompanied by precipitation of pale green crystals. After the absorption ceased (*ca.* 2 hr), the precipitates were filtered, washed successively with cold ether and *n*-hexane, and dried *in vacuo;* 0.11 g (83% yield). Toluene may also be used as a reaction medium. Alternatively, the peroxo complex was prepared in quantitative yield by interaction of oxygen with Ni(*t*-BuNC)$_2$ in ether or tetrahydrofuran. The dried peroxo complex can be kept in a refrigerator indefinitely, but an explosion was sometimes experienced when a completely dried sample was handled at room temperature. The explosion is thought to be caused by the presence of a trace amount of some organic peroxides. To avoid the explosion hazard it seems better to use aromatic hydrocarbon solvents for the preparation with an effort to remove traces of organic impurities. Prolonged storing should be avoided. A freshly prepared sample sealed in a capillary under nitrogen did not start to decompose until the temperature reached about 70°. The instability prevented recrystallization but an analytically pure crystalline sample which appears to be of adequate size for X-ray analysis can be obtained by introduction of oxygen into a cold (below −30°) dilute ether solution (0.2 g of Ni(*t*-BuNC)$_4$ in 40 ml of ether).

Anal. Calcd for $C_{10}H_{18}N_2O_2Ni$: C, 46.7; H, 7.0; O, 12.5; N, 10.9. Found: C, 46.0; H, 7.0; O, 12.9; N, 10.4.

In all cases, the peroxo complex was characterized by means of its ir spectrum (Table II). For the nmr and electronic spectra see Tables I and III, respectively. The magnetic susceptibility χ_m was 9.92×10^{-5} at 77°K and 8.0×10^{-5} (cgs emu) at 298°K, corresponding to a moment of 0.126 BM.

Ni(O$_2$)(cyclo-C$_6$H$_{11}$NC)$_2$ was prepared similarly from Ni(cyclo-C$_6$H$_{11}$NC)$_4$. The pale green crystalline complex was obtained almost quantitatively; it decomposes at 63° under nitrogen.

Anal. Calcd for $C_{14}H_{22}N_2O_2Ni$: C, 54.42; H, 7.40; O, 10.37; N, 9.07. Found: C, 54.5; H, 7.40; O, 10.6; N, 9.05.

Pd(O$_2$)(*t*-BuNC)$_2$ was prepared by introducing dry oxygen into an ether solution (15 ml) of 0.27 g of Pd(*t*-BuNC)$_2$ at −30°. Immediate precipitation of almost colorless fine crystals takes place with oxygen absorption. The precipitates were filtered at −30° under nitrogen and washed with cold ether. The yield was 0.18 g (60%). It starts to decompose if the temperature is raised rapidly, at about 115° under nitrogen. Attempted recrystallization was unsuccessful. However, analytically pure fine needles having a bluish gray shade were obtained when oxygen diluted with nitrogen was slowly introduced into a relatively dilute Pd(*t*-BuNC)$_2$ solution.

Anal. Calcd for $C_{10}H_{18}N_2O_2Pd$: C, 39.65; H, 5.95; O, 10.48; N, 9.11. Found: C, 39.1; H, 5.96; O, 10.3; N, 9.12.

III. **Reactions of Peroxo Complexes.** (a) **Thermal Decomposition of Ni(O$_2$)(*t*-BuNC)$_2$.** Solid Ni(O$_2$)(*t*-BuNC)$_2$ (0.256 g, 1 mmol) was heated at 50° *in vacuo* (10^{-4} mm) for 6 hr to find no appreciable change in the color and also in its ir spectrum. A suspension of Ni(O$_2$)(*t*-BuNC)$_2$ (0.128 g, 0.5 mmol) in 20 ml of dry toluene was stirred under nitrogen at room temperature; the color of the mixture changed from pale green to dark brown. After 24 hr, the mixture was distilled at 20–30° *in vacuo* to afford 0.074 g (0.86 mmol) of *t*-BuNCO and a black residue. The residue was treated with an excess of *t*-BuNC in toluene to give a yellow solution from which was isolated 56 mol % of Ni(*t*-BuNC)$_4$ and a small amount of *t*-BuNCO which was identified as (*t*-BuNH)$_2$CO.

(b) **With Isocyanide.** Ni(O$_2$)(*t*-BuNC)$_2$ (0.257 g, 1 mmol) was treated with an excess of *t*-BuNC (0.83 g, 10 mmol) in dry toluene (10 ml) under nitrogen at room temperature for 8 hr. The initially green suspension turned into a yellow solution, which was distilled *in vacuo* to give a fraction containing 0.158 g (1.6 mmol) of *t*-BuNCO and residues containing Ni(*t*-BuNC)$_4$. Ni(O$_2$)(*t*-BuNC)$_2$ was treated similarly for a few minutes with 4 mol of MeNC or cyclo-C$_6$H$_{11}$NC. The reaction with 4 mol of MeNC produced a mixture of *t*-BuNCO and MeNCO and the reaction with 4 mol of cyclo-C$_6$H$_{11}$NC gave a mixture of *t*-BuNCO and cyclo-C$_6$H$_{11}$NCO; these products were identified as monosubstituted ureas, RNHCONH$_2$.

(c) **With Triphenylphosphine.** Triphenylphosphine (525 mg, 2 mmol) and the oxygen complex (128 mg, 0.5 mmol) were suspended in a toluene–*n*-hexane mixture (15 ml) at −33° under nitrogen. The mixture was warmed up under stirring to room temperature slowly and stirring was continued for 4 hr. Colorless needles of triphenylphosphine oxide (117 mg, 0.42 mmol) were precipitated upon chilling down to −20°. The filtered solution was concentrated under reduced pressure to give 114 mg (0.15 mmol) of orange-yellow crystals identified as Ni(PPh$_3$)$_2$(*t*-BuNC)$_2$ by comparing its ir spectrum with that of the authentic sample[37] prepared by the reaction of Ni(*t*-BuNC)$_2$ with 2 mol of PPh$_3$.

(d) **With Tetracyanoethylene.** To a suspension of TCNE (81.4 mg, 0.64 mmol) in dry toluene (25 ml) was added the oxygen complex (163 mg, 0.64 mmol) under nitrogen at −20°. The reaction mixture was stirred at −20° for 2 hr resulting in a dark red solution with oxygen gas evolution (8.6 ml, 0.36 mmol, 56.3%). Distillation of the solution at room temperature under reduced pressure (3 mm) gave a distillate containing *t*-butyl isocyanate (0.366 mmol, 59.2%). Extraction of the residue with toluene gave Ni(*t*-BuNC)$_2$(TCNE) as brown crystals (87 mg, 38.8%). The yellowish brown insoluble part left after extraction was treated with an excess of *t*-butyl isocyanide in toluene to give Ni(*t*-BuNC)$_3$(TCNE)[32] in good yield. These TCNE complexes were identified by comparing the ir data with those of the authentic samples.

(e) **With Iodine.** Ni(O$_2$)(*t*-BuNC)$_2$, (125 mg, 0.5 mmol) was treated with 1 mmol of iodine in dry toluene (10 ml) under nitrogen at −40°. The color changed upon mixing from green to dark red with concomitant evolution of oxygen (10.8 ml, 90%). The solution was filtered to remove a small amount of insoluble solids. After removal of the solvent *in vacuo*, dark red crystals (97 mg) were obtained and identified by the ir spectrum as NiI$_2$(*t*-BuNC)$_2$.

Similarly Pd(O$_2$)(*t*-BuNC)$_2$ was treated with iodine in toluene; the oxygen gas evolution was almost quantitative. From the solution, PdI$_2$(*t*-BuNC)$_2$, mp 161–162°, was isolated and identified by its ir spectrum.

(f) **With BF$_3$·Et$_2$O.** To a suspension of 0.257 g (1 mmol) of Ni(O$_2$)(*t*-BuNC)$_2$ in 15 ml of dry toluene was added at −70° 2 ml (15.6 mmol) of freshly distilled BF$_3$·Et$_2$O under stirring. The temperature was allowed to slowly reach ambient temperature and stirring was continued for 10 hr at the temperature. Oxygen gas evolution amounted to 20 ml (83 %). From the dark brown reaction mixture was separated a reddish brown solid product whose poor solubility in organic solvents prevented further purification. The ir spectrum (in Nujol) of the product, mp 102–103° dec, showed an NC stretching band at 2240 cm^{-1}, which is quite high compared to the corresponding bands of Ni(*t*-BuNC)$_4$ and even higher than the bands of Ni(O$_2$)(*t*-BuNC)$_2$ (see Table II) and bands at 840 and 715 cm^{-1} (ν_{BF}) indicating the presence of the BF$_3$ moiety in the complex.

IV. **Reaction of "Ni(*t*-BuNC)$_2$" with *t*-BuNCO.** To a solution of 0.056 g (0.25 mmol) of Ni(*t*-BuNC)$_2$ in 10 mg of diethyl ether was added at −40° 0.24 g (0.5 mmol) of *t*-BuNCO. Immediate precipitation of brown solids took place. After standing overnight at −20°, the solids were filtered, washed with ether, and dried keeping the temperature below −30°. The solid product was air sensitive and thermally unstable decomposing below 40°, so elemental analysis was unsuccessful. Evidence for the coordination of 1 mol of *t*-BuNCO to Ni(*t*-BuNC)$_2$ moiety was obtained from the ir spectrum, which shows, instead of the characteristic band (2260 cm^{-1}) of an isocyanate group, strong bands at 2080 and 2000 cm^{-1}. Further evidence was obtained from the reaction of the products (0.021 g) with an excess of *t*-BuNC, which was carried out in toluene at room temperature to recover 98% of the coordinated *t*-BuNCO (0.011 g as (*t*-BuNH)$_2$CO) together with Ni(*t*-BuNC)$_4$. Therefore the brown solid product appears to be a complex of formula Ni(*t*-BuNCO)(*t*-BuNC)$_2$.

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