a ^3E_g ground term. Such a term can be stabilized by positive axial ligands, which emphasizes the importance of further studies in this largely neglected area of ligand chemistry. Aside from the previously discussed case of positive effective axial charges in polymeric complexes, no other systems appear to have been studied in which positive ligands are unequivocally placed in the first coordination sphere. An obvious candidate for this kind of chemistry would be an amine-bridged ligand in which an axial nitrogen fixed in relation to the plane has been quaternized.

It may be possible for high-spin square-planar nickel to exist with a ^3E_g ground term. However, this depends on the π-donor ability of the equatorial ligands. For a purely ionic or σ-bound complex, high-spin square-planar complexes could exist only at the chemical origin, since *S* is infinite and the value of *A* is irrelevant. Such complexes could only have a $^3B_{1g}$ ground term. If, however, the equatorial ligands were strong π donors, the interelectron repulsion in the d_{xz}, d_{yz} orbitals would be increased[26] to the point where the rearrangement to the ^3E_g ground term would occur. In the present formalism, this implies a finite *apparent* value of *S*. That is, the *z* component of the equatorial π-donor orbitals is equivalent to the presence of an axial positive charge and *A* again will have a substantial negative magnitude. It appears to be relevant that recently reported nickel complexes purporting to be high-spin square planar[27] were prepared with π-donating equatorial ligands and display high magnetic moments which would most easily be described with a ^3E_g ground term. The salicylate ligands employed also create a very small Dq_{xy} splitting which further promotes the stabilization of this ground term.

Throughout this treatment, it has been assumed that the spin singlet terms can be ignored. It is obvious from the calculations on these levels that for large values of *Dq* the $^1A_{1g}$ level soon becomes the ground term as *Ds* and *Dt* increase. No high-spin complexes of tetragonal nickel have been observed with *Dq* values greater than about 13 kK.[28] For this reason, as well as the fact that the position of the chemical origin depends on the value of *Dq*, high-spin tetragonal complexes with ^3E_g ground terms are expected only with relatively low values of this parameter. The influence of the spin singlets cannot be predicted with greater precision because of the very large discontinuity in *Dq* when spin pairing occurs. The change in values of 10*Dq* is 3–4 kK[28] because of shortening of the equatorial bond distance and the consequent shift in the chemical origin means that this rearrangement cannot be displayed in a three dimensional diagram.

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Isocyanide–Nickel(0) and –Palladium(0) Complexes Involving Unsaturated Ligands

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Abstract: The complexes ML(*tert*-BuNC)$_3$, ML(*tert*-BuNC)$_2$, and ML$_2$(*tert*-BuNC)$_2$ (L = tetracyanoethylene, fumaronitrile, maleic anhydride, dimethyl maleate, azobenzene, dimethyl acetylenedicarboxylate, and diphenylacetylene) have been prepared; all three complex types were prepared for M = Ni, but for M = Pd only complexes of formula ML(*tert*-BuNC)$_2$ were isolated. Ir and ^{1}H nmr data have been used to suggest structures for the complexes in solution. For many of the complexes ML(*tert*-BuNC)$_2$, the ir NC stretching frequencies (a and b modes) increase linearly with an increase in the electronegativity of L. A plot of the stretch–stretch interaction [$\Delta\nu$(a–b)] against the electron affinity of L appears to provide an even better measure of metal–ligand back-bonding.

A few transition metal complexes have been proven to be versatile for the preparation of a wide variety of compounds containing an olefin, acetylene, or related π acid. Among such complexes are Vaska's complexes of iridium(I)[1-3] and the tertiary phosphine complexes of platinum(0).[4] Study of the ir CO stretching frequencies for complexes incorporating unsaturated molecules linked to Vaska's compounds has provided important information on the bonding of the unsaturated ligand to the metal. An approximate linear relation between ν_{CO} and the electron affinity of the unsaturated ligand has been observed and discussed[5,6] on the basis of the Dewar–Chatt–Duncanson (DCD) model of bonding.[7a,b] Such an argument is relevant only if the complexes are isostructural, since

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Table I. Properties and Analytical Data

Complexes[a]	Color	Mp,[b] °C	% carbon		% hydrogen		% nitrogen		Mol wt	
			Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
Ni(TCNE)(*tert*-BuNC)$_3$	Purple	130–134[c] dec	57.82	58.63	6.24	6.51	22.47	22.51	432	421[d]
Ni(FN)(*tert*-BuNC)$_3$	Red	125–128	59.16	59.16	7.57	7.42	18.12	17.75	385	355[e]
Ni(MA)(*tert*-BuNC)$_3$	Reddish brown	142–143	56.18	55.66	7.20	7.09	10.35	10.14	405	363[e]
Ni(TCNE)(*tert*-BuNC)$_2$	Brown	164–167 dec	54.43	55.04	5.13	5.68	23.79	23.26		
Ni(FN)(*tert*-BuNC)$_2$	Yellow	124–126	55.49	55.18	6.65	6.77	18.48	17.84	302	314[e]
Ni(MA)(*tert*-BuNC)$_2$	Orange-yellow	114–116	52.05	51.81	6.24	6.07				
Ni(DM)(*tert*-BuNC)$_2$	Orange	118–120	52.06	51.56	7.10	6.93	7.57	6.97		
Ni(PhN=NPh)(*tert*-BuNC)$_2$	Red	163–164	64.75	64.75	6.93	6.91	13.76	13.65		
Ni(PhC≡CPh)(*tert*-BuNC)$_2$	Yellow	125–127 dec	71.49	71.39	7.00	6.71	6.95	6.78		
Ni(MA)$_2$(*tert*-BuNC)$_2$	Red	140	51.10	51.40	5.26	5.45	6.65	6.32	420	337[e]
Ni(CO)$_2$(*tert*-BuNC)$_2$	Colorless	56[c]	51.32	51.12	6.43	6.58	9.03	8.67	280	265
Pd(TCNE)(*tert*-BuNC)$_2$	Yellow	145 dec	47.95	48.13	4.50	4.42	20.98	20.54		
Pd(FN)(*tert*-BuNC)$_2$	Colorless	142–143	47.94	47.89	5.74	5.84	15.96	16.18	350	384[d]
Pd(MA)(*tert*-BuNC)$_2$	Colorless	119–120	45.35	45.57	5.44	5.46	7.55	7.58		
Pd(DM)(*tert*-BuNC)$_2$	Colorless	100–102	46.11	46.34	6.29	6.28	6.72	6.75		
Pd(PhC≡CPh)(*tert*-BuNC)$_2$	Colorless	139–143 dec	63.93	64.15	6.26	6.16	6.21	6.03		

[a] Abbreviations for ligands are: TCNE = tetracyanoethylene, FN = fumaronitrile, MA = maleic anhydride, DM = dimethyl maleate. [b] Measured in a sealed tube filled with nitrogen unless otherwise noted. [c] Measured in air. [d] Measured by vapor pressure osmometry using benzene. [e] Measured cryoscopically in benzene.

ν_{CO} will be sensitive to the location of CO relative to the other ligands. In fact, addition of tetracyanoethylene (TCNE) or oxygen to Vaska's complex leads to complexes with different alignments of ligands, *i.e.*, IrBr(TCNE)(CO)(PPh$_3$)$_2$[8] and IrCl(O$_2$)(CO)(PPh$_3$)$_2$,[9] and the "low" position of oxygen in the relationship between ν_{CO} and the electron affinity may then be related to the difference in stereochemistry.[1] Some tertiary phosphine complexes of Pt(0), Pd(0), or Ni(0) are very reactive toward π acids, but the resulting complexes of formula M(L)(PR$_3$)$_2$ lack a functional group such as CO which provides convenient vibrational data.

Recently we have found a ready access to tetrakis- or bisisocyanide complexes of nickel(0) and palladium(0), and we have shown that these complexes take up an oxygen molecule.[10] The compounds M(*tert*-BuNC)$_2$ and M(*tert*-BuNC)$_4$ are very reactive toward a wide variety of electrophilic reagents, and complexes of three different formulas, ML(*tert*-BuNC)$_3$, ML(*tert*-BuNC)$_2$, and ML$_2$(*tert*-BuNC)$_2$ (L = olefin and other π acids), have been obtained. The isocyanide ligands in the complexes provide distinct vibrational and ^{1}H nmr spectral data, and consequently it is possible to suggest probable ligand geometries for most of the complexes, including a novel azobenzene complex Ni(PhN=NPh)(*tert*-BuNC)$_2$.[11] The vibrational data are useful for understanding not only the metal–olefin or metal–acetylene bonding but also the mode of attachment of other small molecules, in particular molecular oxygen, to the same metal systems.[10] We shall examine the relationship between ir NC stretching frequencies of the *tert*-BuNC ligands and the electron-accepting properties of olefinic ligands in ML(*tert*-BuNC)$_2$. Particularly interesting is the coordination of azobenzene and of acetylenic compounds. Azobenzene incorporates lone-pair orbitals that might affect the bonding of this ligand to a metal, while an acetylenic bond incorporates a set of π_g and π_u (out of plane) orbitals orthogonal to the π_g and π_u (in plane) orbitals that lie in the plane involving the metal and the two carbon atoms. The (out of plane) π orbitals of an acetylene may participate in bonding to the metal, thus making the bonding scheme much more complicated than that in olefin–metal complexes. The DCD description of bonding for olefinic complexes has been applied to acetylenic complexes,[12–14] and total energies of several acetylene complexes of Pt(0) were calculated to infer an appropriate hybridization scheme for the central metal[13] as well as the most stable configuration.[14] The calculations led to the conclusion that the out-of-plane π interaction in Pt(0) complexes increases the stability of the acetylene coordination. It is therefore of interest to use the vibrational data to examine if this is valid for the present complexes of Ni(0) and Pd(0).

Results and Discussion

Preparative Chemistry. Table I lists the complexes prepared and shows their colors, melting points, and analytical data.

(1) ML(*tert*-BuNC)$_3$. An activated olefin such as tetracyanoethylene (TCNE), maleic anhydride (MA), or fumaronitrile (FN) reacts with Ni(*tert*-BuNC)$_4$ under mild condition affording the appropriate tris(isocyanide) complex, NiL(*tert*-BuNC)$_3$. A weaker electron acceptor such as ethylene, diphenylacetylene, or azobenzene fails to replace the isocyanide ligand, and Ni(*tert*-BuNC)$_4$ is recovered unchanged. This electrophilic feature is common for ligand exchange in the reactions of ML$_4$ with L′ (M = Ni(0), Pd(0), and Pt(0)[4]). An S$_\text{N}$1 mechanism has been established for the reaction of Ni[P(OC$_2$H$_5$)$_3$]$_4$ with C$_6$H$_{11}$NC[15] and of Ni(CO)$_4$ with CO, P(C$_6$H$_5$)$_3$,[16] or various phosphines and phosphites.[17] In the last reaction, however, Tolman[17] claimed that

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Table II. Ir Spectra of NiL(*tert*-BuNC)$_3$

	$\nu_{N\equiv C}$, cm^{-1}		
	Nujol	Benzene	Other bands, cm^{-1}
Ni(TCNE)(*tert*-BuNC)$_3$[a]	2185, 2163, 2155	2182, 2153	$\nu_{C\equiv N}$ 2223, 2212
Ni(FN)(*tert*-BuNC)$_3$	2149, 2120, 2115	2152, 2113, 2075 sh[b]	$\nu_{C\equiv N}$ 2220
Ni(MA)(*tert*-BuNC)$_3$	2150, 2110, 2108	2157, 2110, 2078 (sh)[b]	$\nu_{C=O}$ 1788, 1720

[a] Free *tert*-BuNC (liquid film) exhibits $\nu_{N\equiv C}$ at 2130 cm^{-1} (vs). [b] A very weak band probably assignable to the ^{13}C isotopic splitting of $\nu_{N\equiv C}$.

steric effects play a dominant role. Dissociative equilibria have been established for Pt(PPh$_3$)$_3$.[18,19]

The molecular weight in benzene of Ni(*tert*-BuNC)$_4$ (found, 307; calcd, 391) clearly indicates its dissociation in solution. A rapid ligand exchange between Ni(*tert*-BuNC)$_4$ and free *tert*-BuNC detected by the ^{1}H nmr spectrum in benzene is then intelligible in terms of an S$_N$1 process involving three-coordinate species, since a five-coordinate intermediate is unlikely for such a bulky ligand as *tert*-BuNC. Thus the formation of NiL(*tert*-BuNC)$_3$ probably involves a first-order dissociative equilibrium followed by the attack of an olefin. However, the reluctance of azobenzene toward reaction 1 cannot be rationalized in this way since FN, MA, and azobenzene are comparable in electron affinity.

$$\mathrm{Ni}(tert\text{-}\mathrm{BuNC})_4 \rightleftharpoons \mathrm{Ni}(tert\text{-}\mathrm{BuNC})_3 + tert\text{-}\mathrm{BuNC} \qquad (1a)$$

$$\mathrm{Ni}(tert\text{-}\mathrm{BuNC})_3 + \mathrm{L} \longrightarrow \mathrm{NiL}(tert\text{-}\mathrm{BuNC})_3 \qquad (1b)$$

Some trisisocyanide complexes can also be derived from the corresponding bisisocyanide complex (*vide infra*).

$$\mathrm{NiL}(tert\text{-}\mathrm{BuNC})_2 + tert\text{-}\mathrm{BuNC} \longrightarrow \mathrm{NiL}(tert\text{-}\mathrm{BuNC})_3$$
$$\mathrm{L} = \mathrm{TCNE, FN, MA} \qquad (2)$$

Neither tetrakisisocyanide nor trisisocyanide complexes are available for palladium(0), and all efforts to prepare complexes of formula PdL(*tert*-BuNC)$_3$ from PdL(*tert*-BuNC)$_2$ and *tert*-BuNC were fruitless.

(2) ML (*tert*-BuNC)$_2$. Complexes of this formula are best prepared from a cluster complex "Ni(*tert*-BuNC)$_2$"[20] or from a binuclear complex "Pd (t-BuNC)$_2$."[20] They are versatile complexes capable of reacting with a variety of compounds including O$_2$[10], RX, TCNE, FN, MA, PhC≡CPh, CS$_2$,[20] etc. Such activated olefins as TCNE, FN, MA, or dimethyl maleate (DM) can replace the acetylene or carbon disulfide ligand in complexes ML(*tert*-BuNC)$_2$ (L = PhC≡CPh or CS$_2$[20]), resulting in the corresponding bisisocyanide complex, *e.g.*

$$\text{“}\mathrm{Ni}(tert\text{-}\mathrm{BuNC})_2\text{”} + \mathrm{L} \longrightarrow \mathrm{NiL}(tert\text{-}\mathrm{BuNC})_2 \qquad (3)$$

$$\mathrm{Ni(CS_2)}(tert\text{-}\mathrm{BuNC})_2 + \mathrm{L} \longrightarrow \mathrm{NiL}(tert\text{-}\mathrm{BuNC})_2 + \mathrm{CS_2}$$
$$\mathrm{L} = \mathrm{TCNE, FN, MA} \qquad (4)$$

(3) ML$_2$(*tert*-BuNC)$_2$. The bis(maleic anhydride) complex Ni(MA)$_2$(*tert*-BuNC)$_2$ can be prepared in good yield from "Ni(*tert*-BuNC)$_2$." Unexpectedly, other strong dπ acceptors such as TCNE or a moderate acceptor such as FN, PhN=NPh, or PhC≡CPh failed to afford this type of complex, NiL(*tert*-BuNC)$_2$ being the only isolable product. Addition of TCNE to Ni(TCNE)(*tert*-BuNC)$_2$ did not occur. This was also the case for the diphenylacetylene complex; Ni(PhC≡CPh)$_2$(*tert*-BuNC)$_2$ was not formed. Addition of an excess of allene to the suspension of "Ni(*tert*-BuNC)$_2$" in cold *n*-hexane or benzene produces an unstable species, Ni(allene)$_2$(*tert*-BuNC)$_2$.[20] However, extensive dissociation of this complex prevented its isolation in pure form.

$$\text{“}\mathrm{Ni}(tert\text{-}\mathrm{BuNC})_2\text{”} + 2\mathrm{MA} \longrightarrow \mathrm{Ni(MA)_2}(tert\text{-}\mathrm{BuNC})_2 \qquad (5)$$

It has been reported that substitution reactions of Ni(CO)$_4$ with isocyanides give the complexes Ni(CO)$_n$(RNC)$_{4-n}$.[21] The reaction with 2 mol (or slightly more) of *tert*-BuNC yielded predominantly Ni(CO)$_2$(*tert*-BuNC)$_2$ without appreciable formation of complexes of other composition, *e.g.*, Ni(CO)(RNC)$_3$ or Ni(CO)$_3$(RNC).

Attempts to prepare Pd(CO)$_n$(RNC)$_{4-n}$ have failed and no indication was obtained even *in situ* for the formation.

Properties and Structure. (1) NiL(*tert*-BuNC)$_3$. The complexes of formula NiL(*tert*-BuNC)$_3$ (L = TCNE, MA, and FN) are moderately air sensitive in solution; the TCNE complex, which is quite inert even in solution, is an exception. Their ir and ^{1}H nmr spectra (Tables II and III) suggest approximately the same configuration for these three complexes.

Table III. Nmr Spectra of NiL(*tert*-BuNC)$_3$[a]

	τ, ppm	
	Olefinic protons	*tert*-Butyl protons
Ni(TCNE)(*tert*-BuNC)$_3$		9.03 (s)
Ni(TCNE)(*tert*-BuNC)$_3$ + TCNE		9.03 (s)
Ni(TCNE)(*tert*-BuNC)$_3$ + 2-*tert*-BuNC[b]		9.04 (s)
Ni(FN)(*tert*-BuNC)$_3$[c]	6.79 (s)	9.00 (s)
Ni(MA)(*tert*-BuNC)$_3$	5.61 (s)	9.00 (s)
Ni(MA)(*tert*-BuNC)$_3$ + MA[d]	4.98 (s)	8.78 (s)
Ni(MA)(*tert*-BuNC)$_3$ + 2-*tert*-BuNC	5.54 (s)	8.99 (s)

[a] Measured in benzene using TMS as internal reference. [b] The free *tert*-BuNC shows a triplet at τ 9.05 in benzene. [c] Free fumaronitrile shows a resonance at τ 5.40 in benzene. [d] Free maleic anhydride shows a resonance at τ 4.56 in benzene.

(a) Ni(TCNE)(*tert*-BuNC)$_3$. The two NC stretching vibrations observed in benzene solution indicate a C_{3v} alignment of the isocyanide ligands. The ^{1}H nmr spectrum shows one sharp singlet for *tert*-butyl protons; the equivalence requires either intramolecular rotation of the olefinic ligand (eliminating the anisotropic effect) or rapid exchange of ligands through a dissociative mechanism. Dissociation of the TCNE ligand can be

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Table IV. Ir and Nmr Spectra of ML(*tert*-BuNC)$_2$

	Ir, cm^{-1} [a]		Nmr, ppm[b]	
	$\nu_{N\equiv C}$	Other	$\tau_{tert\text{-}Bu}$	τ_{olefin}
Ni(O$_2$)(*tert*-BuNC)$_2$	2196, 2178		8.59[c]	
Ni(TCNE)(*tert*-BuNC)$_2$	2194, 2179	$\nu_{C\equiv N}$ 2222, 2219	9.08	
Ni(PhN=NPh)(*tert*-BuNC)$_2$	2168, 2140	δ_{C-H} 756, 690	8.51 (9)[d]	2.80 (3)[d,e] 3.15 (2)[d,e]
Ni(FN)(*tert*-BuNC)$_2$	2162, 2138	$\nu_{C\equiv N}$ 2199	9.12 (9)	7.55 (1)
Ni(MA)(*tert*-BuNC)$_2$	2159, 2118	$\nu_{C=O}$ 1799, 1730	9.08 (9)	6.19 (1)
Ni(DM)(*tert*-BuNC)$_2$	2154, 2120	$\nu_{C=O}$ 1708, 1675	9.06 (9)	6.45 (1)
Ni(CH$_3$O$_2$CC≡CCO$_2$CH$_3$)(*tert*-BuNC)$_2$[f]	2160, 2123	$\nu_{C\equiv C}$ 1830 $\nu_{C=O}$ 1690, 1678		
Ni(PhC≡CPh)(*tert*-BuNC)$_2$	2138, 2100	$\nu_{C\equiv C}$ 1810 ν_{C-H} 762, 693	8.47 (9)[d]	2.35 (2)[d,e] 2.71 (3)[d,e]
Pd(O$_2$)(*tert*-BuNC)$_2$	2207, 2190		8.51[c]	
Pd(TCNE)(*tert*-BuNC)$_2$	2220, 2210	$\nu_{C\equiv N}$ 2226	8.93	
Pd(FN)(*tert*-BuNC)$_2$	2182, 2162	$\nu_{C\equiv N}$ 2205	9.16 (9)	6.98 (1)
Pd(MA)(*tert*-BuNC)$_2$	2178, 2156	$\nu_{C=O}$ 1805, 1732	9.12 (9)	5.93 (1)
Pd(DM)(*tert*-BuNC)$_2$	2160, 2140	$\nu_{C=O}$ 1710, 1673	9.11 (9)	6.07 (1)
Pd(CH$_3$O$_2$CC≡CCO$_2$CH$_3$)(*tert*-BuNC)$_2$[f]	2177, 2158	$\nu_{C\equiv C}$ 1807 $\nu_{C=O}$ 1690, 1680		
Pd(PhC≡CPh)(*tert*-BuNC)$_2$	2150, 2125	$\nu_{C\equiv C}$ 1825 δ_{C-H} 762, 695	8.42 (9)[d]	2.22 (2),[d,e] 2.67 (3)[d,e]

[a] Measured in Nujol mull. [b] Measured in benzene unless otherwise stated, using TMS as internal reference. Both *tert*-butyl and olefinic protons were observed as sharp singlets. Values in parentheses show relative intensities. [c] Measured in CDCl$_3$. [d] Measured in acetone-*d*$_6$. [e] Aromatic protons, complex multiplet. [f] Crude products.

excluded, since addition of free TCNE does not affect the *tert*-butyl proton resonance (Table III). However, upon addition of free *tert*-BuNC, the resonance gives rise to only one singlet at τ 9.04, implying rapid isocyanide ligand exchange. The molecular weight measured in benzene (see Table I) indicates that the dissociation of *tert*-BuNC ligands occurs only to a very small extent. Since only two NC stretching vibrations are observable, a species such as Ni(TCNE)(*tert*-BuNC)$_2$ (*vide infra*) does not exist to any significant extent. However, the presence of a small amount of Ni(TCNE)(*tert*-BuNC)$_2$ would be sufficient to cause effective equilibration of the *tert*-butyl protons.

Generally the NC stretching frequencies are lower than those of the bisisocyanide complex, NiL(*tert*-BuNC)$_2$ (Tables II and IV), a feature suggestive of less effective π back-bonding to the olefin ligand in a trigonal-pyramidal structure than in a nearly planar structure. This view is supported by the ^{1}H nmr data (Tables III and IV) which indicate that the olefinic protons of NiL(*tert*-BuNC)$_2$ are generally more effectively shielded than are those of NiL(*tert*-BuNC)$_3$.

(b) **Ni(MA)(*tert*-BuNC)$_3$ and Ni(FN)(*tert*-BuNC)$_3$.** The ir NC bands (a and e modes) of these two complexes in the solid state show patterns similar to the spectrum of Ni(TCNE)(*tert*-BuNC)$_3$. A cryosocopic molecular weight measurement (Table I) suggests a little more enhanced dissociation in solution in comparison with Ni(TCNE)(*tert*-BuNC)$_3$. As addition of either free maleic anhydride or free *tert*-BuNC to a solution of Ni(MA)(*tert*-BuNC)$_3$ causes equilibration of the olefinic protons (Table III), the dissociation may take place in two processes (eq 6 and 7).

$$\mathrm{Ni(MA)}(tert\text{-}\mathrm{BuNC})_3 \rightleftharpoons \mathrm{Ni}(tert\text{-}\mathrm{BuNC})_3 + \mathrm{MA} \quad (6)$$

$$\mathrm{Ni(MA)}(tert\text{-}\mathrm{BuNC})_3 \rightleftharpoons \mathrm{Ni(MA)}(tert\text{-}\mathrm{BuNC})_2 + tert\text{-}\mathrm{BuNC} \quad (7)$$

(2) **ML(*tert*-BuNC)$_2$.** Mononuclear complexes of this formula (L = TCNE, MA, FN, DM, PhN=NPh, and PhC≡CPh) are very air sensitive, particularly in solution. Generally the palladium complexes appear to be more thermally stable than the nickel analogs. Table IV lists the ir and nmr spectral data.

(a) **M(TCNE)(*tert*-BuNC)$_2$.** The molecular structure of Ni(TCNE)(*tert*-BuNC)$_2$ has been studied by a three-dimensional, single-crystal X-ray analysis[22] which showed a trigonal structure (the TCNE molecule being considered as a single ligand) with a considerable dihedral angle of 23° between the Ni–C$_2$ (of TCNE) and the Ni–C$_2$ (of *tert*-BuNC) planes. The two NC stretching vibrations (a and b mode) are close to those in the corresponding dioxygen complexes, implying comparable electron drainage into the TCNE and dioxygen ligands. From the ir data we anticipate an approximately trigonal structure for the palladium complex, Pd(TCNE)(*tert*-BuNC)$_2$.

(b) **M(FN)(*tert*-BuNC)$_2$.** The NC stretching frequencies lie between those of M(TCNE)(*tert*-BuNC)$_2$ and M(PhC≡CPh)(*tert*-BuNC)$_2$ (Table IV). Not unexpectedly,[23] semiempirical caluculations of the total energies of platinum(0) complexes[14] that are similar to the present compounds indicated a minimum in energy for the square-planar form and a monotonic increase to a maximum for the pseudotetrahedral form. It is generally observed for complexes ML(*tert*-BuNC)$_2$ that the higher the NC stretching frequencies, the greater the stability of the olefin–metal bonding. This implies importance of π bonding in the metal-to-olefin bonding. We then expect a greater dihedral angle for Ni(FN)(*tert*-BuNC)$_2$ than for Ni(TCNE)(*tert*-BuNC)$_2$. The palladium analog, Pd(FN)(*tert*-BuNC)$_2$, however, may be less twisted from the planar structure in view of the electronic property of the palladium metal.

The nmr and vibrational data for Ni(FN)(*tert*-BuNC)$_3$ (Tables II and III) also indicate ineffective back-bonding to the olefinic ligand compared to that in Ni(FN)(*tert*-BuNC)$_2$ (Table IV).

(c) **M(MA)(*tert*-BuNC)$_2$ and M(DM)(*tert*-BuNC)$_2$.** The ir and ^{1}H nmr data of these complexes being similar to those of the fumaronitrile complexes, similar stereo-

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(22) J. K. Stalick and J. A. Ibers, *J. Amer. Chem. Soc.*, **92**, 5333 (1970).

(23) A number of X-ray structures of stable Pt(0)–olefin or –acetylene complexes are nearly square planar; see, *e.g.*, L. Manojlovic-Muir, K. W. Muir, and J. A. Ibers, *Discuss. Faraday Soc.*, No. 47, 84 (1969); W. H. Baddley, *Inorg. Chim. Acta*, **2**, 7 (1968 .

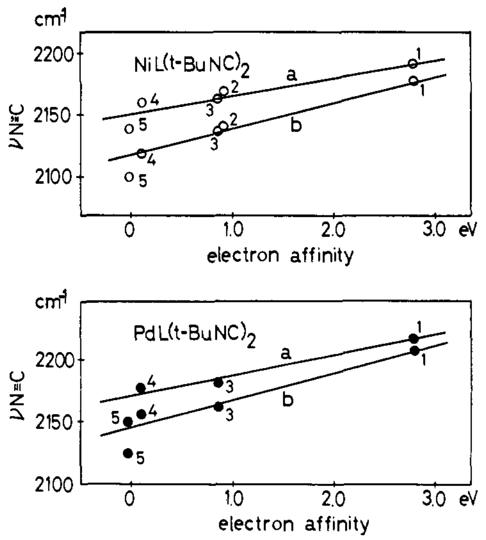
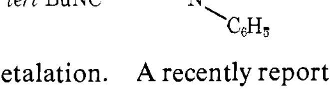


Figure 1. Relationship between ν_{NC} and electron affinity; 1 = TCNE, 2 = PhN = NPh, 3 = FN, 4 = MA, 5 = PhC≡CPh. References for the electron affinity data: TCNE and FN, A. C. Farragher and A. M. Page, *Trans. Faraday Soc.*, **63**, 2369 (1967); PhN=NPh, B J. Tabner and J. R. Yandle, *J. Chem. Soc. A*, 381 (1968); MA, C. H. J. Wells, *Tetrahedron*, **22**, 1985 (1966); PhC≡CPh, J. E. Lovelock, A. Zlatkis, and R. S. Becker, *Nature (London)*, **193**, 540 (1962), **183**, 731 (1962).

chemistries are anticipated. The ν_{NC} stretching frequencies are higher in the palladium complexes than in the nickel analogs, and the olefinic protons are less shielded in the palladium complexes (Table IV). The CO stretching frequencies of the carboxylic group in the nickel and palladium complexes are comparable and are lower than those of the free ligand.

(d) Ni(PhN=NPh)(*tert*-BuNC)₂. The ir spectrum contained strong CH out-of-plane deformation bands at 756 and 690 cm^{-1} similar to those (777 and 690 cm^{-1}) of free azobenzene, but no other band was observed in this region. This indicates the absence of species such as an ortho metal-substituted azobenzene.[24] Since two NC stretching absorptions are observed, and since each of the NC frequencies (a and b modes) lies on the line of the frequency *vs.* electron affinity plot (Figure 1), a stereochemistry similar to the other olefin complexes can be anticipated. Consistently, the nmr spectrum (Table IV) showed two aromatic proton resonances with an intensity ratio 2:3. A number of transition metal complexes of azo compounds have been reported,[25] but to date this is the only reported example in which azobenzene forms a side-on (olefin like) coordination



without ortho metalation. A recently reported complex Mo(PhN=NPh)(π-C_5H_5)$_2$[26] may belong to this category, but the bonding of the azo linkage to the metal is rather inert to substitution reactions with various π acids. Substitution of an azobenzene ligand in Ni(PhN=NPh)(*tert*-BuNC)₂ can be effected readily with molecular oxygen or TCNE. This substitution also

$$\text{Ni(PhN=NPh)}(\textit{tert}\text{-BuNC})_2 + O_2 \longrightarrow \text{Ni}(O_2)(\textit{tert}\text{-BuNC})_2 + \text{PhN=NPh} \quad (8)$$

constitutes strong evidence for the olefin-like ligation involving no ortho metalation.

It should be noted that despite the presence of the filled nonbonding (lone pair) orbitals, azobenzene acts as a fairly efficient dπ acceptor for nickel(0) species.

(e) M(XC≡CX)(*tert*-BuNC)₂ (X = Ph, COOCH₃). The acetylene complexes of Ni(0) and Pd(0) provide well-defined spectral data, except Ni($CH_3OOCC{\equiv}CCOOCH_3$)(*tert*-BuNC)₂, whose ir spectrum measured with much difficulty was of somewhat lower resolution. The NC stretching bands of M(PhC≡CPh)(*tert*-BuNC)₂ (M = Ni, Pd) strongly suggest that the acetylene is the weakest acceptor of any monounsaturated moiety examined here. The plot of ν_{NC} *vs.* electron affinity (Figure 1) clearly demonstrates that the electron drainage to the acetylene ligand is much less than expected. A closely related observation is that the carbonyl stretching frequency (2018 cm^{-1}) for IrCl(NCC≡CCN)(CO)(PPh₃)₂ is lower than that (2029 cm^{-1}) for the fumaronitrile complex, IrCl(NCCH=CHCN)(CO)(PPh₃)₂.[6] These data are difficult to account for with electronic effects only, and are incompatible with the conclusion from the molecular orbital calculations on Pt(0) complexes that both in-plane and out of-plane π bonding serve to stabilize the acetylene coordination.[14]

The NC stretching frequencies are approximately comparable among the Ni(0) complexes of dimethyl acetylenedicarboxylate and of dimethyl maleate, while the frequencies of Pd($CH_3O_2CC{\equiv}CCO_2CH_3$)(*tert*-BuNC)₂ are definitely higher than those of Pd($CH_3O_2CCH{=}CHCO_2CH_3$)(*tert*-BuNC)₂ (Table IV). This last trend is the one compatible with theory.[14] Thus far, available data are insufficient to draw any conclusion regarding the exact nature of bonding of acetylene to metal.

The stereochemistries of these complexes are unknown. We tentatively consider these acetylene complexes to have a structure analogous to that of Ni(TCNE)(*tert*-BuNC)₂. If one accepts the interpretation of the favorable configuration of Pt(acetylene)L₂ in terms of the MO approach,[13,14] a considerable dihedral angle would be anticipated between the MC₂ and ML₂ planes in such a complex as M(PhC≡CPh)(*tert*-BuNC)₂. This view receives support from the known X-ray data; *e.g.*, 14° for Pt(PhC≡CPh)(PPh₃)₂[27] and 8° for Pt(NCC≡CCN)(PPh₃)₂.[28]

It may be added that the system NiL(*tert*-BuNC)₂ functions as an active catalyst for polymerization of acetylenes including dimethyl acetylenedicarboxylate.[20] In general Pd(acetylene)(*tert*-BuNC)₂ is more labile than the nickel congener. Pd(PhC≡CPh)(*tert*-BuNC)₂ is particularly labile, and isolation of the pure complex is only possible when the crystallization is performed at lower temperatures in the presence of free diphenyl-

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(24) A. C. Cope and R. W. Siekman, *J. Amer. Chem. Soc.*, **87**, 3272 (1965).

(25) (a) S. Otsuka, T. Yoshida, and A. Nakamura, *Inorg. Chem.*, **8**, 2514 (1969); (b) R. P. Bennett, *ibid.*, **9**, 2184 (1970); (c) D. L. Weaver *ibid.*, **9**, 2250 (1970); (d) R. F. Heck, *J. Amer. Chem. Soc.*, **90**, 313 (1968); (e) M. I. Bruce, M. Z. Iqbal, and F. G. A. Stone, *J. Chem. Soc. A*, 3204 (1970), and references therein.

(26) S. Otsuka, A. Nakamura, and H. Minamida, *Chem. Commun.*, 1148 (1969).

(27) J. O. Glanville, J. M. Stewart, and S. O. Grim, *J. Organometal. Chem.*, 7, 9 (1967).

(28) C. Panattoni and R. Graziani in "Progress in Coordination Chemistry," M. Cais, Ed., Elsevier, Amsterdam, 1968, p 310.

acetylene. Diphenylacetylene also failed to form a stable complex with $IrCl(CO)(PPh_3)_2$, and dimethyl acetylenedicarboxylate formed an easily dissociated complex with Vaska's compound.[29]

The relatively weak bonding of acetylene to the metals renders the complex valuable for preparative reactions. Thus molecular oxygen immediately reacts with the complex in solution below −40°.

$$M(PhC{\equiv}CPh)(\textit{tert}\text{-}BuNC)_2 + O_2 \longrightarrow M(O_2)(\textit{tert}\text{-}BuNC)_2 + PhC{\equiv}CPh \quad (9)$$

$$M = Ni, Pd$$

(3) **ML_2 (*tert*-BuNC)$_2$.** The Ni complexes are soluble in most organic solvents and are monomeric in solution. The thermal stability varies to a great extent depending upon the ligand.

(a) **$Ni(CO)_2$(*tert*-BuNC)$_2$.** The thermal stability of this complex appears to be fairly good compared to $Ni(CO)_4$ and Ni(*tert*-BuNC)$_4$, and its stability to air is better than the Ni(*tert*-BuNC)$_4$. The ir spectrum contains NC stretching frequencies at 2150 and 2110 cm^{-1}, which are close to those of Ni(MA)(*tert*-BuNC)$_3$, and carbonyl stretching frequencies at 2000 and 1962 cm^{-1} which are lower than the value (2037 cm^{-1}) for $Ni(CO)_4$.[30a] These ir data suggest a pseudotetrahedral alignment to be the most reasonable stereochemistry. Comparisons of ν_{NC} between Ni(*tert*-BuNC)$_4$ and $Ni(CO)_2$(*tert*-BuNC)$_2$ and of ν_{CO} for $Ni(CO)_2$(*tert*-BuNC)$_2$, $Ni(CO)_2(PPh_3)_2$,[30b] and $Ni(CO)_4$ indicate the following $d\pi$ accepting strengths: PPh_3 < *tert*-BuNC < CO.

(b) **$Ni(MA)_2$(*tert*-BuNC)$_2$.** As three types of maleic anhydride complexes are now available, comparative spectral data are of interest. The NC stretching frequencies increase in the order Ni(MA)(*tert*-BuNC)$_3$ < Ni(MA)(*tert*-BuNC)$_2$ < $Ni(MA)_2$(*tert*-BuNC)$_2$ (Tables II and IV), indicating maleic anhydride to be a stronger $d\pi$ electron acceptor than *tert*-BuNC. Consistently, a similar trend is observable in the CO stretching frequencies. The nmr spectra of the olefinic protons of these three complexes indicate considerable upfield shifts compared to the chemical shift of free maleic anhydride (τ 4.56), but there is no simple trend in chemical shifts among the three complexes. Presently it is impossible to predict the stereochemistry of the complexes, but at least the observation of two NC stretching bands excludes a trans-planar structure (D_{2h}). In view of the considerable electron transfer to two maleic anhydride ligands, a somewhat twisted planar structure is more likely than a pseudotetrahedral structure. The structure seems reasonable, as maleic anhydride is a stronger acceptor than the carbon monoxide ligand (ν_{NC} = 2185 and 2170 cm^{-1} for $Ni(MA)_2$(*tert*-BuNC)$_2$ and 2150 and 2110 cm^{-1} for $Ni(CO)_2$(*tert*-BuNC)$_2$).

Isocyanide Stretching Vibrations and Bonding. For cis-planar complexes (C_{2v}), it is claimed that the ir frequency of the a_1 mode is higher than that of the b_1 mode.[30c] If the symmetry is reduced from C_{2v} to C_2, the two ir-active modes become a and b. In local symmetry C_2, one cannot *a priori* expect this assignment to be valid. On the basis of the following observation, we assign the two NC stretching bands. Figure 1 clearly indicates that each band of the two vibrational modes correlates linearly with the electron affinity of the ligand L in ML (*tert*-BuNC)$_2$. The separation between the two bands corresponds to the stretch–stretch interaction between the two NC stretching vibrations. Figure 1 further indicates that the separation increases with the decrease in NC frequencies, *i.e.*, with the increase in electron drainage into the isocyanide ligands. Moreover, the higher band is less sensitive than the lower one to the electronic properties of the olefinic ligand. The higher and lower bands are assignable to the a and b modes, respectively, since a valence-bond description of vibration indicates that the symmetrical vibration will not be efficient for the cis-type stretch–stretch vibrational interactions. Although calculations of interaction force constants involve an assumption of a simplified force field,[31,32] which has been a subject of dispute,[33,34] it was established for a series of nickel carbonyl derivatives $NiL_2(CO)_2$[35] that the lower the ν_{CO} values the higher the interaction force constants.

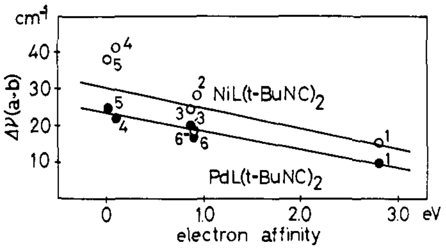

Figure 2. Relationship between $\Delta\nu$(a–b) and electron affinity; 6 = O_2 (for the electron affinity value for O_2, see ref 36): ○, nickel complexes; ●, for palladium complexes.

A notable exception to the linear correlation between ν_{NC} and the electron affinity data is again the oxygen molecule; the ν_{NC} values (see Table IV) fall in a region higher than expected from the accepted electron affinity value (0.87 eV[36]). The "high" values contrast with "low" values observed for Vaska's oxygen complex.

Figure 1 suggests that the difference in frequencies between the two modes, $\Delta\nu$(a–b) will correlate with the electron affinity. In fact, a linear relationship exists for the palladium system PdL(*tert*-BuNC)$_2$ including the oxygen and diphenylacetylene complexes (Figure 2). The nickel system, in particular complexes of weak $d\pi$ acceptors, deviates considerably from the linearity. The large structural change, *i.e.*, twisting of the dihedral angle, in the nickel system is probably responsible for the deviation. It is rather surprising to observe the linear relationship for PdL(*tert*-BuNC)$_2$ despite the large variation in bonding schemes. We therefore propose the use of $\Delta\nu$(a–b) as a measure of the effective back-bonding of a ligand in complexes such as the present one. The bonding scheme for acetylene or oxygen coordination, of course, also depends on the central metal. It may be relevant to point out here that the dative "forward" bonding of both the in-plane and out-of-plane filled π_u orbitals has been invoked for the stable complex, $WL(RC{\equiv}CR)_3$.[37,38]

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[29] J. P. Collman and J. W. Kang, *J. Amer. Chem. Soc.*, **89**, 844 (1967).

[30] D. M. Adams, "Metal-Ligand and Related Vibrations," Arnold, London, 1967: (a) p 120; (b) p 156; (c) p 100.

[31] F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, **84**, 4432 (1962).

[32] F. A. Cotton, A. Musco, and G. Yagupsky, *Inorg. Chem.*, **6**, 1357 (1967).

[33] L. H. Jones, *ibid.*, 7, 1681 (1968).

[34] F. A. Cotton, *ibid.*, 7, 1683 (1968).

[35] G. R. Van Hecke and W. Horrocks, Jr., *ibid.*, **5**, 1960 (1966).

[36] V. I. Vedeneyev, *et al.*, "Bond Energies, Ionization Potentials and Electron Affinities," Arnold, London, 1966, p 195.

Experimental Section

^{1}H nmr spectra were measured on a 100-Mc Model JNM 4H-100 instrument from Japan Electron Optics Laboratories, using TMS as an internal reference. Ir spectra of samples were recorded in Nujol mulls on a Hitachi Perkin-Elmer Model 225. Molecular weight measurements were made cryoscopically or by vapor pressure osmometry using benzene as solvent. All reactions and physical measurements were carried out in a nitrogen atmosphere. Ni(*tert*-BuNC)$_4$, "Ni(*tert*-BuNC)$_2$," and "Pd(*tert*-BuNC)$_2$" were prepared by known methods.[10] Analytical data and some physical properties of the complexes described below are listed in Table I.

Tris(*tert*-butyl isocyanide)tetracyanoethylenenickel(0). Tetracyanoethylene (102 mg, 0.8 mmol) was added to a solution of tetra(*tert*-butyl isocyanide)nickel (300 mg, 0.77 mmol) in toluene (10 ml) at ambient temperature. A dark red color developed instantly. Concentration of the resulting solution gave purple crystals, which were recrystallized from CHCl$_3$ (303 mg, 91%). The compound is very stable in air, but decomposes with evolution of *tert*-butyl isocyanide at 130°.

Alternatively, *tert*-butyl isocyanide (0.1 ml, 0.9 mmol) was added to a solution of Ni(TCNE)(*tert*-BuNC)$_2$ (73 mg, 0.17 mmol) in benzene (10 ml) at ambient temperature. After 3 hr at 25°, the dark red solution was concentrated *in vacuo* to give the complex quantitatively.

Tris(*tert*-butyl isocyanide)fumaronitrilenickel(0). A solution of fumaronitrile (156 mg, 2.1 mmol) in benzene (5 ml) was added to a mixture of tetra(*tert*-butyl isocyanide)nickel (790 mg, 2.1 mmol) and benzene (15 ml). A dark red color developed immediately. After 1 hr at ambient temperature, the mixture was concentrated *in vacuo* to give red solids. Recrystallization from a mixture of toluene–*n*-hexane gave red cubic crystals (560 mg, 73%). The compound is stable in air for several minutes.

Alternatively, *tert*-butyl isocyanide (0.2 ml, *ca.* 1.8 mmol) was added to a yellow solution of Ni(FN)(*tert*-BuNC)$_2$ (115 mg, 0.38 mmol) in benzene (5 ml) at ambient temperature, and the mixture was stirred for 1 hr at 25° to give the complex quantitatively.

[Tris(*tert*-butyl isocyanide)maleic anhydride]nickel(0). Maleic anhydride (113 mg, 1.16 mmol) was added to a solution of tetra(*tert*-butyl isocyanide)nickel (450 mg, 1.16 mmol) in benzene (10 ml) at ambient temperature. Brown crystals appeared in a few minutes. Recrystallization from a mixture of toluene–*n*-hexane afforded air-sensitive reddish brown needles (240 mg, 51%). This was the only product even when a large excess of maleic anhydride was employed for the reaction.

Alternatively, *tert*-butyl isocyanide (40 mg, 0.48 mmol) was added to a reddish orange solution of Ni(MA)(*tert*-BuNC)$_2$ (100 mg, 0.24 mmol) in benzene (5 ml) at ambient temperature to give a brownish red solution from which the complex was isolated quantitatively.

Bis(*tert*-butyl isocyanide)tetracyanoethylenenickel(0). To a red solution of [bis(*tert*-butyl isocyanide)carbon disulfide]nickel (63 mg, 0.21 mmol) in benzene (10 ml) was added tetracyanoethylene (51 mg, 0.4 mmol) at ambient temperature. After stirring for 2 hr at ambient temperature, the red-brown solution was concentrated *in vacuo* to give brown solids which were washed with ether to remove unchanged tetracyanoethylene. Recrystallization from toluene gave air-stable reddish brown crystals (63 mg, 86%).

Alternatively, the complex was obtained in quantitative yield by treating bis(*tert*-butyl isocyanide)nickel (140 mg, 0.6 mmol) with tetracyanoethylene (102 mg, 0.8 mmol) in benzene at ambient temperature.

Bis(*tert*-butyl isocyanide)fumaronitrilenickel(0). A mixture of fumaronitrile (95 mg, 1.2 mmol) and bis(*tert*-butyl isocyanide)nickel (136 mg, 0.61 mmol) in *n*-hexane (15 ml) was stirred at 5°, and then the temperature was allowed to reach ambient temperature within 0.5 hr. Yellowish orange solids appeared in the solution and were filtered and subsequently recrystallized from ether to give yellow crystals (90 mg, 44%). The complex is extremely air sensitive. Addition of a large excess of fumaronitrile did not produce Ni(FN)$_2$(*tert*-BuNC)$_2$.

[Bis(*tert*-butyl isocyanide)maleic anhydride]nickel(0). Maleic anhydride (126 mg, 1.28 mmol) was added to a stirred solution of bis(*tert*-butyl isocyanide)nickel (288 mg, 1.28 mmol) in ether (20 ml) at 5°. After 1 hr at ambient temperature, the mixture was cooled to −70° to give yellow crystals. Recrystallization from ether gave pure yellowish orange crystals (230 mg, 56%); recrystallization from toluene–*n*-hexane produced an impure sample contaminated with Ni(MA)$_2$(*tert*-BuNC)$_2$. This is an extremely air-sensitive compound, but it does not decompose under nitrogen at −20° for several months.

[Bis(*tert*-butyl isocyanide)dimethyl maleate]nickel(0). Dimethyl maleate (180 mg, 1.25 mmol) was added to a stirred solution of bis(*tert*-butyl isocyanide)nickel (281 mg, 1.25 mmol) in ether (25 ml) at 5°. After stirring for 2 hr at ambient temperature, the orange solution was concentrated *in vacuo* to give orange solids. Recrystallization from a mixture of ether and *n*-hexane gave orange needles (262 mg, 57%). The complex is very air sensitive.

Bis(*tert*-butyl isocyanide)azobenzenenickel. A solution of azobenzene (58 mg, 0.32 mmol) and bis(*tert*-butyl isocyanide)nickel (72 mg, 0.32 mmol) in ether (20 ml) was stirred at 25° for 3 hr to produce orange-red precipitates. After removal of the solvent *in vacuo*, the precipitates were washed with *n*-hexane, dried *in vacuo*, and recrystallized from ether, affording the complex as red needles in almost quantitative yield. The complex decomposes at 162°, and is extremely air sensitive in the solid state.

Bis(*tert*-butyl isocyanide)diphenylacetylenenickel(0). A solution of diphenylacetylene (45 mg, 0.254 mmol) in ether (5 ml) was added to a solution of bis(*tert*-butyl isocyanide)nickel (57 mg, 0.254 mmol) in ether (15 ml), and the mixture was stirred at 25° for 1 hr. The color of the bis(*tert*-butyl isocyanide)nickel solution rapidly turned from red to yellow. Concentration *in vacuo* of the yellow solution gave yellow solids which were recrystallized from *n*-hexane, affording yellow needles in quantitative yield, which decomposed at 125–127°.

Reaction of Dimethyl Acetylenedicarboxylate with Ni(PhC≡CPh)(*tert*-BuNC)$_2$. To a solution of Ni(PhC≡CPh)(*tert*-BuNC)$_2$ (343 mg, 0.85 mmol) in 30 ml of ether was added dimethyl acetylenedicarboxylate (121 mg, 0.85 mmol) at −78°. A fine yellow precipitate appeared upon addition of cold *n*-hexane at −78°, but isolation in pure form was hampered by a tendency toward polymerization to form dark brown untractable polymerizates at room temperature. The replacement of diphenylacetylene with dimethyl acetylenedicarboxylate in the crude yellow complex was confirmed by the ir spectrum which shows CO stretching bands and the NC stretching frequencies higher than those of the starting complex (Table IV).

Bis(*tert*-butyl isocyanide)bis(maleic anhydride)nickel(0). A mixture of maleic anhydride (235 mg, 2.40 mmol) and bis(*tert*-butyl isocyanide)nickel (270 mg, 1.20 mmol) in ether (20 ml) was stirred at ambient temperature for 3 hr to afford orange-red crystals which were recrystallized from a mixture of toluene and *n*-hexane (246 mg, 49%). Exposure to air decomposes the compound within a few minutes.

Alternatively, a solution of maleic anhydride (40 mg, 0.4 mmol) in benzene (1 ml) was added to a suspension of [bis(*tert*-butyl isocyanide)carbon disulfide]nickel (61 mg, 0.2 mmol) in *n*-hexane (5 ml), and the mixture was stirred for 1.5 hr at 30° to give the complex quantitatively.

Bis(*tert*-butyl isocyanide)dicarbonylnickel(0). *tert*-Butyl isocyanide (183 mg, 0.23 ml, 2.1 mmol) was added to a solution of nickel carbonyl (171 mg, 1 mmol) in *n*-hexane (10 ml) at room temperature and stirred for 5 hr (CO gas evolved). The complex was obtained as white needles from the concentrated solution in quantitative yield. The compound is moderately stable in air, mp 58–59°, without decomposition.

Bis(*tert*-butyl isocyanide)tetracyanoethylenepalladium(0). A mixture of tetracyanoethylene (141 mg, 1.1 mmol) and bis(*tert*-butyl isocyanide)palladium (272 mg, 1 mmol) in toluene (20 ml) was stirred at −20° for 5 hr. The initial orange color of the solution turned to yellow. Concentration of the resulting solution gave yellow crystals (decomposition at 145°) which were recrystallized from toluene (320 mg, 80%). The compound was moderately stable in air.

Bis(*tert*-butyl isocyanide)fumaronitrilepalladium(0). A mixture of bis(*tert*-butyl isocyanide)palladium (153 mg, 0.56 mmol) and fumaronitrile (87 mg, 1.12 mmol) in benzene (15 ml) was stirred at ambient temperature. After 1 hr at 30°, the colorless solution was concentrated *in vacuo* to give a colorless oil which crystallized upon addition of *n*-hexane. Recrystallization from a mixture of benzene and *n*-hexane gave colorless needles (113 mg, 57%). The compound is stable to air for several days.

[Bis(*tert*-butyl isocyanide)maleic anhydride]palladium(0). Maleic anhydride (50 mg, 0.5 mmol) was added to a suspension of bis(*tert*-butyl isocyanide)palladium (140 mg, 0.5 mmol) in *n*-hexane (10 ml) at 5°. Colorless crystals appeared immediately. Recrystallization from a mixture of toluene and *n*-hexane gave colorless

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(37) D. P. Tate, J. M. Augl, W. M. Ritchey, B. L. Ross, and J. G. Frasselli, *J. Amer. Chem. Soc.*, **86**, 3261 (1964).

(38) R. B. King, *Inorg. Chem.*, 7, 1044 (1968).

needles (123 mg, 82%). The complex was moderately stable in air. Similar treatment of maleic anhydride (70 mg, 0.7 mmol) with [bis(*tert*-butyl isocyanide)carbon disulfide]palladium (112 mg, 0.34 mmol) in *n*-hexane (10 ml) at ambient temperature afforded the complex (60 mg, 48%).

[Bis(*tert*-butyl isocyanide)dimethyl maleate]palladium(0). Dimethyl maleate (135 mg, 0.94 mmol) was added to a suspension of bis(*tert*-butyl isocyanide)palladium (255 mg, 0.94 mmol) in ether (20 ml) below −20° and the mixture was stirred for 3 hr at −20–0°. The orange suspension turned into a colorless solution. After stirring 1 hr at ambient temperature, the colorless solution was concentrated *in vacuo* to give a colorless oil which solidified upon addition of *n*-hexane. Recrystallization from a mixture of ether and *n*-hexane gave colorless needles (326 mg, 83%). The complex was moderately stable in air.

Bis(*tert*-butyl isocyanide)diphenylacetylenepalladium(0). A solution of diphenylacetylene (196 mg, 1.1 mmol) in *n*-hexane (15 ml) was added to a suspension of bis(*tert*-butyl isocyanide)palladium (272 mg, 1 mmol) in a mixture of *n*-hexane (20 ml) and ether (15 ml) below −20°, and the suspension was stirred for several hours below −20°. The orange color of the suspension turned to yellowish white. The white precipitate was filtered off, washed with chilled ether (10 ml), and dried *in vacuo* below 0°. When dissolved in ether at 25° this compound decomposed owing to dissociation followed by irreversible reaction (*vide infra*). Recrystallization from ether in the presence of 1 mol of free diphenylacetylene below 0° gave the complex as white microcrystals (0.360 g, 80%) which decompose at 116°. This compound was not too air sensitive in the solid state but was unstable in solution. A complicated solution chemistry is involved, because dissociation produces a highly coordinatively unsaturated species, Pd(*tert*-BuNC)$_2$, which tends to polymerize into polynuclear compounds.

Reaction of Dimethyl Acetylenedicarboxylate with Pd(PhC≡CPh)(*tert*-BuNC)$_2$. To a solution of Pd(PhC≡CPh)(*tert*-BuNC)$_2$ (250 mg, 0.55 mmol) in ether (50 ml) was added dimethyl acetylenedicarboxylate (78 mg, 0.55 mmol) at −78°. Colorless needles appeared upon addition of *n*-hexane at −78°. Thermal instability prevented further purification. The ir spectrum of the crude product (Table IV) indicates coordination of dimethyl acetylenedicarboxylate to the Pd(*tert*-BuNC)$_2$ moiety. At ambient temperature the colorless solution containing the crude complex rapidly turned into a red solution which gave only intractable materials.

Reaction of Bis(*tert*-butyl isocyanide)diphenylacetylenenickel(0) with Molecular Oxygen. Dry oxygen was introduced into a solution of bis(*tert*-butyl isocyanide)diphenylacetylenenickel in ether at −30°. Immediately, a pale green precipitate appeared. The pale green compound was identified by its infrared spectrum as the known oxygen complex, Ni(O$_2$)(*tert*-BuNC)$_2$.[10] Evaporation of the mother liquors to dryness *in vacuo* gave a white solid identified as diphenylacetylene by its infrared spectrum and melting point.

Reaction of Bis(*tert*-butyl isocyanide)azobenzenenickel(0) with Molecular Oxygen. Introduction of dry oxygen into a solution of bis(*tert*-butyl isocyanide)azobenzenenickel in ether at −30° afforded Ni(O$_2$)(*tert*-BuNC)$_2$ and azobenzene.

Similarly, treatment with dry oxygen of a solution of bis(*tert*-butyl isocyanide)diphenylacetylenepalladium in ether produced the oxygen complex Pd(O$_2$)(*tert*-BuNC)$_2$[10] and diphenylacetylene, both of which were identified by their ir spectra.

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Nickel(II) and Nickel(IV) Complexes of 2,6-Diacetylpyridine Dioxime

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Abstract: The preparation and properties of bis(2,6-diacetylpyridine dioxime)nickel(II) perchlorate, sodium bis(2,6-diacetylpyridine dioximato)nickelate(II), and bis(2,6-diacetylpyridine dioximato)nickel(IV) are reported. Indirect evidence indicates that the oxidized complex contains a high oxidation state of nickel rather than cation-stabilized radical ligands. The electronic and proton nmr spectra of the Ni(II) complexes and extended Hückel molecular orbital calculations of the protonated and unprotonated ligand are used to support a model which accounts for the ease of oxidation of the anionic Ni(II) complex and the stability toward oxidation of the protonated species. The model proposed stresses the importance of high-energy ligand orbitals of σ symmetry and the relative unimportance of the ligand π system in the stabilization of high oxidation states of nickel.

Although there has been considerable interest in the stabilization of high oxidation states of first-row transition metals, few Ni(IV) complexes have been reported, and of these, the claim is dubious in several instances. The reported examples may be divided into three general classifications—classical six-coordinate, planar four-coordinate, and "sandwich" compounds. In the first group, vicinal aliphatic dioximes (DH_2)[2] and trimeric formaldoxime (FoH_3)[3] are reported to form complexes of the type M_2NiD_3 and $M_2Ni(Fo)_2$ ($M =$ Na, K), respectively. Heteropoly compounds such as $Na_{12}NiNb_{12}O_{38}$[4] and $Ba_3NiMo_9O_{32}\cdot 12H_2O$[5] and mixed oxides such as $BaNiO_3$[6] and $MNiIO_6\cdot H_2O$[7] contain Ni(IV) in an O_6 environment. Other classical six-coordinate complexes include M_2NiF_6,[8] and a claim is made for $[Ni(diars)_2Cl_2]Cl_2$.[9] Planar four-coordinate complexes originally reported to contain Ni(IV), but about which there is considerable doubt, include bis complexes with ligands of types I and II.[10] Recently, an X-

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