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Aromatic Nitroso Compounds as π Acids in the Zerovalent Nickel Triad Metal Complexes and the Metal-Assisted Atom-Transfer Reactions with Donor Reagents

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Mono- and trinuclear arylnitroso complexes of the nickel triad, M(ArNO)(t-BuNC)$_2$ [M = Ni, Ar = p-XC$_6$H$_4$ (X = NMe$_2$, OMe, Me, H, Cl, Br), 3,4-Cl$_2$C$_6$H$_3$; M = Pd, Ar = p-ClC$_6$H$_4$], M(PhNO)(PPh$_3$)$_2$ (M = Ni, Pd, Pt), and Pd$_3$(PhNO)$_3$L$_3$ [L = P(t-Bu)$_3$, PPh(t-Bu)$_2$], have been prepared. Ir data of the mono- and trinuclear compounds suggest a side-on η^2 coordination of the N=O group which has been confirmed by an x-ray analysis on the latter compound. For M(ArNO)(t-BuNC)$_2$, the N≡C stretching frequencies (A' and A'' modes) correlate linearly with the Hammett σ constant (σ_p) of the para substituent. Consistently a linear correlation was found between the upfield shift ($\Delta\tau$) of meta protons and the cis stretch–stretch interaction $\Delta\nu$(N≡C). The property of nitrosobenzenes as two-center π acids has been discussed on the basis of the spectral data. Facile N—O bond cleavage of the coordinated PhNO leading to phenylnitrene and oxygen atom transfer was observed when Ni(PhNO)(t-BuNC)$_2$ was treated with electron-donating reagents, t-BuNC, PPh$_3$, and PhNO. The reaction of PhNO with t-BuNC to give t-BuNCO, PhN=N(O)Ph, and PhN=C=N(t-Bu) can be carried out as a catalytic process. Metal-catalyzed atom-transfer reactions between the nitro compound and t-BuNC were also described.

In most of the nitrosobenzene[1,2] or substituted nitrosobenzene complexes[3,4] so far prepared the ligand coordinates to a metal as a σ base through the N or O atom, although conclusive evidence for their structures is lacking. A recent x-ray study of *trans*-PdCl$_2$(PhNO)$_2$ revealed η^1 coordination through the N atom.[5] The –NO group in the nitroso compound, isoelectronic (12 electrons) to dioxygen, should be able to act as a two-center π acid. There has been only one example, Fe$_2$(CO)$_6$(3-Cl-2-CH$_3$C$_6$H$_3$NO)$_2$,[6] for which η^2 coordination has been established.[7] We were interested in obtaining a series of mononuclear transition metal compounds having an η^2-ligated nitroso compound for information on the nature of their bonding. In such an attempt we obtained a stable trinuclear compound Pd$_3$(PhNO)$_3$[P(t-Bu)$_3$]$_3$ and reported briefly the x-ray structure.[8] In this paper we describe the preparation of mononuclear compounds of the type M(η^2-nitrosobenzene)L$_2$ (M = Ni, Pd, Pt; L = t-BuNC, PPh$_3$) and their spectroscopic data relevant to a discussion of the bonding to metal. The spectral properties suggestive of considerable perturbation of the NO bond upon coordination prompted us to study the reactivity of coordinated nitroso compounds. Nitrosobenzenes are considerably reactive. For example, the deoxygenation occurs readily with trivalent phosphorus compounds leading to nitrene reactions.[9] This type of reaction was also observed with Fe(salen) (salen = N,N'-ethylenebis(salicylaldiminato)).[10] Some metal-assisted atom-transfer redox reactions were also reported without details.[11,12]

$$\begin{array}{l} \mathrm{ArNO} + \mathrm{L} \rightarrow \mathrm{ArN{:}} + \mathrm{LO} \\ \qquad\qquad\quad \downarrow \mathrm{L'} \\ \qquad\qquad\quad \mathrm{ArNL'} \end{array}$$

From the reactivity studies, we were able to convert a stoichiometric atom-transfer reaction into a catalytic process.

Results and Discussion

Preparation, Properties, and Structure. The complex Ni(t-BuNC)$_n$[13] (n = 2 or 4) suspended in n-hexane was treated with an equimolar amount of p-XC$_6$H$_4$NO (X = Me$_2$N, MeO, Me, H, Cl, Br) or 3,4-Cl$_2$C$_6$H$_3$NO at room temperature to obtain quantitatively diamagnetic complexes Ni(ArNO)(t-BuNC)$_2$ as red microcrystals. The reaction with an excess of PhNO under nitrogen gave unexpectedly a nitrobenzene complex Ni(PhNO$_2$)(t-BuNC)$_2$.[12] A similar reaction of "Pd(t-BuNC)$_2$"[13] with p-ClC$_6$H$_4$NO yields a diamagnetic orange complex Pd(p-ClC$_6$H$_4$NO)(t-BuNC)$_2$. Triphenylphosphine analogues M(PhNO)(PPh$_3$)$_2$ (M = Ni, Pd, Pt) are prepared from M(CH$_2$=CH$_2$)(PPh$_3$)$_2$[14-16] and PhNO in n-hexane. In contrast, a similar reaction of the two-coordinate phosphine complex PdL$_2$[17] (L = P(t-Bu)$_3$, PPh(t-Bu)$_2$) affords a trinuclear complex Pd$_3$(PhNO)$_3$L$_3$[8] as red crystals with liberation of 1 mol of phosphine. The steric bulk of P(t-Bu)$_3$ (cone angle[18] 180 ± 2°) and PPh(t-Bu)$_2$ (cone angle[19] 170 ± 2°) apparently prevents the formation of Pd(PhNO)L$_2$.

The isocyanide complexes M(ArNO)(t-BuNC)$_2$ are monomeric and readily soluble in benzene, ether, and acetone but insoluble in saturated hydrocarbons. The nickel isocyanide complexes are unstable in air and even in the solid state, while the palladium complex is stable in the solid state for a few hours. The triphenylphosphine complexes are less soluble in benzene and more stable toward air compared to the isocyanide analogues. The trinuclear complexes Pd$_3$(PhNO)$_3$L$_3$ are soluble in n-hexane and stable in air in solution. The thermal stability of the nickel isocyanide complexes increases with increase of electron-accepting property of the para substituent of the nitroso compounds, as manifested qualitatively in their decomposition temperatures (Table I).

Assignment of the N=O stretching of nitrosobenzenes appears not to have been settled yet. The absorption at ~1500 cm^{-1} has been assigned as ν(N=O),[21] while Nakamoto et al.[22] assigned the absorption at 1340–1350 cm^{-1} as ν(N=O). The ir spectra of the coordinated nitrosobenzenes (Table II), lacking absorptions in these regions, show a new strong band in a region of 978–1040 cm^{-1}. These bands were not observed in *trans*-PdCl$_2$(PhNO)$_2$[2] where PhNO coordinates as a ni-

Table I. Properties and Analytical Data of Nitrosobenzene Complexes

	Color	Dec pt,[a] °C	Anal.,[b] % C	H	N
Ni(3,4-$Cl_2C_6H_3NO$)-(*t*-BuNC)$_2$	Red	130–135	48.17 (47.91)	5.32 (5.27)	10.42 (10.47)
Ni(*p*-ClC_6H_4NO)-(*t*-BuNC)$_2$	Red	120	53.21 (52.43)	6.13 (6.05)	11.13 (11.46)
Ni(*p*-BrC_6H_4NO)-(*t*-BuNC)$_2$	Red	108	46.29 (46.75)	5.35 (5.39)	9.92 (10.22)
Ni(PhNO)(*t*-BuNC)$_2$[c]	Red	111	58.56 (57.87)	7.02 (6.98)	12.88 (12.64)
Ni(*p*-MeC_6H_4NO)-(*t*-BuNC)$_2$	Red	113	59.42 (58.99)	7.24 (7.28)	11.94 (12.20)
Ni(*p*-$MeOC_6H_4NO$)-(*t*-BuNC)$_2$	Red	92	56.03 (56.39)	6.87 (6.96)	
Ni(*p*-$Me_2NC_6H_4$-NO)(*t*-BuNC)$_2$	Red	40	57.31 (57.63)	7.56 (7.52)	14.32 (14.94)
Pd(*p*-ClC_6H_4NO)-(*t*-BuNC)$_2$	Orange	113–118	46.62 (46.38)	5.31 (5.35)	9.93 (10.13)
Ni(PhNO)(PPh_3)$_2$	Violet	109–110	72.62 (73.03)	5.21 (5.11)	2.24 (2.03)
Pd(PhNO)(PPh_3)$_2$	Orange-red	119–122	68.39 (68.34)	4.64 (4.78)	1.98 (1.89)
Pt(PhNO)(PPh_3)$_2$	Yellow	151–154	61.15 (61.01)	4.22 (4.27)	1.62 (1.69)
$Pd_3(PhNO)_3$[P(*t*-Bu)$_3$]$_3$	Red	195–199[d]	52.02 (51.97)	7.83 (7.76)	3.36 (3.36)
$Pd_3(PhNO)_3$[PPh-(*t*-Bu)$_2$]$_3C_6H_6$[e]	Red	189–190[d]	56.74 (57.20)	7.06 (6.54)	3.26 (3.03)

[a] Measured in a sealed tube filled with nitrogen. [b] Required values are shown in parentheses. [c] Molecular weight measured cryoscopically in benzene was 343 (required value 331). [d] Measured in air. [e] Molecular weight measured by vpo in benzene was 1301 (required value 1307).

Table II. Ir Spectra (cm^{-1}) of Nitrosobenzene Complexes

	ν(N–O)[a]	ν(N≡C)[b]
Ni(3,4-$Cl_2C_6H_3NO$)(*t*-BuNC)$_2$	1036	2175.0, 2143.0
Ni(*p*-ClC_6H_4NO)(*t*-BuNC)$_2$	1026	2173.3, 2139.6
Ni(*p*-BrC_6H_4NO)(*t*-BuNC)$_2$	1040	2172.0, 2138.0
Ni(PhNO)(*t*-BuNC)$_2$	1032 (1038)	2172.4, 2137.8
Ni(*p*-MeC_6H_4NO)(*t*-BuNC)$_2$	1030	2170.2, 2135.6
Ni(*p*-$MeOC_6H_4NO$)(*t*-BuNC)$_2$	1029	2168.3, 2133.9
Ni(*p*-$Me_2NC_6H_4NO$)(*t*-BuNC)$_2$	1030	2166.0, 2130.5
Pd(*p*-ClC_6H_4NO)(*t*-BuNC)$_2$	1040	2182,[a] 2162[a]
Ni(PhNO)(PPh_3)$_2$	1025 (1027)	
Pd(PhNO)(PPh_3)$_2$	1039	
Pt(PhNO)(PPh_3)$_2$	973	
$Pd_3(PhNO)_3$[P(*t*-Bu)$_3$]$_3$	1043	
$Pd_3(PhNO)_3$[PPh(*t*-Bu)$_2$]$_3$	1039	

[a] Measured in Nujol mull. The values measured in benzene-d_6 are shown in parentheses. [b] Measured in benzene.

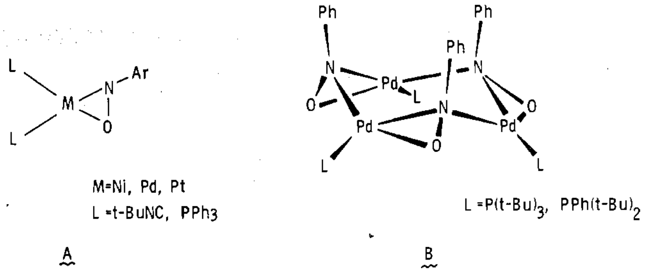

Figure 1. Structures of $M(ArNO)L_2$ (A) and $Pd_3(PhNO)_3$ (B).

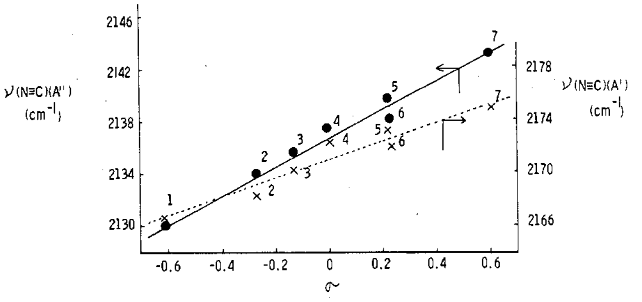

Figure 2. Relationship between ν(N≡C) and Hammett σ constants: 1, *p*-Me_2N; 2, *p*-MeO; 3, *p*-Me; 4, *p*-H; 5, *p*-Cl; 6, *p*-Br; 7, 3,4-Cl_2.

trogen σ base. As is evident from the ν(N—O) values observed for a series of Ni(substituted nitrosobenzene)(*t*-BuNC)$_2$ complexes, no apparent linear correlation exists between the frequency and Hammett's σ constants,[23] perhaps due to strong couplings between the several vibrational modes. The frequency dependent on the metal identity decreases in an order of Pt < Ni < Pd, a trend known for C≡C and O—O stretchings in acetylene[24,25] and dioxygen complexes,[26] respectively. Thus the new band is assignable to the N—O vibration and its stretching frequency corresponds to the N—O bond order of about 1.[27] The two strong N≡C stretching absorptions of the nickel isocyanide complexes at 2130–2175 cm^{-1} (in benzene) suggest cis ligation of the isocyanides. This is also the case for Pd(*p*-ClC_6H_4NO)(*t*-BuNC)$_2$ (Table II). From these ir data η^2 coordination of the N═O group forming a triangular structure (A, Figure 1) is inferred for complexes $M(ArNO)L_2$ (M = Ni, Pd; L = *t*-BuNC, PPh_3). The coordination of nitrosobenzenes as two-center π acids is evident from the upfield shift of aromatic ring protons on coordination (Table III), since the downfield shift is expected for η^1 coordination through the N or O atom. This bonding scheme of nitrosobenzenes has been confirmed by an x-ray study for $Pd_3(PhNO)_3$[P(*t*-Bu)$_3$]$_3$[8] where the nitrogen atoms act as a bridging ligand through the lone-pair electrons to form the trinuclear complexes (B, Figure 1). The molecule $Pd_3(PhNO)_3$[P(*t*-Bu)$_3$]$_3$ forms "inner" –Pd–N six- and "outer" –Pd–O–N–" nine-membered rings; the latter has C_3 symmetry.[8] The *tert*-butyl protons of $Pd_3(PhNO)_3$[PPh(*t*-Bu)$_2$]$_3$ show AB pattern signals as two doublets at τ 8.69 and 8.43 ($^3J_{H-P}$ = 13.0 Hz) in benzene-d_6 reflecting the diastereotopic nature of two *tert*-butyl groups in PPh(*t*-Bu)$_2$ bonded to the chiral (Pd–N–O)$_3$ ring, while $Pd_3(PhNO)_3$[P(*t*-Bu)$_3$]$_3$ shows, not unexpectedly, a single *tert*-butyl proton signal at τ 8.45 ($^3J_{H-P}$ = 12.0 Hz).

The ^1H NMR spectra of the mononuclear isocyanide complexes (Table III) measured in acetone-d_6 show a sharp singlet at τ 8.5 for *tert*-butyl protons. The equivalence of two *tert*-butyl groups requires an intramolecular rotation of the planar complex or a rapid ligand exchange with rates falling in the NMR time scale. The *tert*-butyl proton signal of a 1:2 mixture of Ni(*p*-ClC_6H_4NO)(*t*-BuNC)$_2$ and free *t*-BuNC shows a sharp singlet at τ 8.58 which is slightly upfield compared to that of Ni(*p*-ClC_6H_4NO)(*t*-BuNC)$_2$ (τ 8.53), suggesting a rapid exchange of *t*-BuNC.

Assignment of two N≡C stretching modes is readily made:[28] the higher stretching band to A' and the lower one to the A'' mode. A linear correlation exists between Hammett's σ constants (σ_p) of para substituents[23] of nitrosobenzene and the N≡C stretching frequencies (A' and A'') of the complexes (Figure 2). Consequently, the cis stretch–stretch interaction [Δν(N≡C)(A'—A'')] also correlates linearly with the Hammett constant. A similar relationship between the electron affinity of the ligand and each frequency of two N≡C stretching modes has been observed for ML(*t*-BuNC)$_2$ (M = Ni, Pd; L = olefins, azobenzene).[28,29]

The parallel behavior confirms our inference regarding nitrosobenzenes as two-center π acids. As Table IV indicates, nitrosobenzenes are comparable to fumaronitrile and azobenzene in their π acidity.

Table III shows the observed and calculated chemical shifts of the ring protons of free and complexed para-substituted

Scheme I

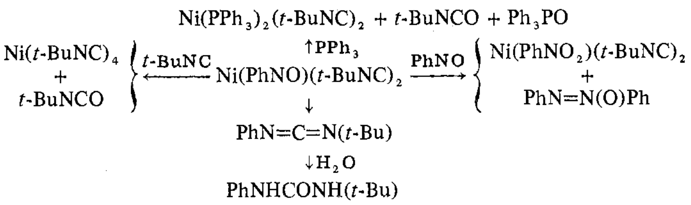

Table III. ^{1}H NMR Spectra (τ) of M(ArNO)(t-BuNC)$_2$^{a}

	Complexed ligand					Free ArNO ligand				$\Delta\tau^c$	
	t-Bu	CH$_3$	H$_o$^{b}	H$_m$^{b}	$J_{H_oH_m}$, Hz	CH$_3$	H$_o$^{b}	H$_m$^{b}	$J_{H_oH_m}$, Hz	H$_o$	H$_m$
Ni(3,4-Cl$_2$C$_6$H$_3$NO)(t-BuNC)$_2$	8.52		2.68^d	2.83^d			2.05^d				
Ni(p-BrC$_6$H$_4$NO)(t-BuNC)$_2$	8.53		2.88 (2.81)	2.68 (2.70)	10.0		2.01 (2.09)	2.13 (2.22)	9.0	0.87	0.55
Ni(p-ClC$_6$H$_4$NO)(t-BuNC)$_2$	8.54		2.78 (2.75)	2.90 (2.80)	9.0		2.03 (2.03)	2.20 (2.32)	9.5	0.75	0.70
Ni(PhNO)(t-BuNC)$_2$	8.53		2.63–3.07^d				2.2^d				
Ni(p-MeC$_6$H$_4$NO)(t-BuNC)$_2$	8.53	7.80	2.82 (2.72)	3.09 (2.95)	8.0	7.54	1.90 (2.03)	2.55 (2.47)	9.0	0.92	0.54
Ni(p-MeOC$_6$H$_4$NO)(t-BuNC)$_2$	8.54	6.25	2.69 (2.73)	3.23 (3.16)	7.5	6.02	2.09 (2.01)	2.83 (2.78)	9.0	0.60	0.40
Ni(p-Me$_2$NC$_6$H$_4$NO)(t-BuNC)$_2$	8.53	7.14	2.74 (2.86)	3.44 (3.62)	9.0	6.82	2.25 (2.14)	3.20 (3.14)	9.5	0.49	0.24
Pd(p-ClC$_6$H$_4$NO)(t-BuNC)$_2$	8.48		2.71	2.91	9.5		2.03	2.20	9.5	0.68	0.71

^{a} Measured in acetone-d_6 or acetone using TMS as internal reference. The values in parentheses are the chemical shifts calculated using the evaluated shielding constants of NO or $-\overline{\mathrm{N{-}O{-}Ni}}(t\text{-BuNC})_2$ (see text). ^{b} H$_o$ and H$_m$ represent protons at ortho and meta positions with respect to the NO and $-\overline{\mathrm{N{-}O{-}Ni}}(t\text{-BuNC})_2$ groups. ^{c} Upfield shifts of ring proton on complexation. ^{d} Multiplet unassignable.

Table IV. N≡C Stretchings (cm^{-1})^a of Nitrosobenzene and Related Complexes, ML(t-BuNC)$_2$^{28}

	Ni		Pd	
L	ν(N≡C)	$\Delta\nu$-(N≡C)^b	ν(N≡C)	$\Delta\nu$-(N≡C)^b
O$_2$	2196, 2178	18	2207, 2190	17
TCNE	2194, 2179	15	2220, 2210	10
p-ClC$_6$H$_4$NO	2170, 2145	25	2182, 2162	20
PhN=NPh	2168, 2140	28		
FN^c	2162, 2138	24	2182, 2162	20
p-Me$_2$NC$_6$H$_4$NO	2162, 2131	31		
MA^d	2159, 2118	41	2178, 2156	22
PhC≡CPh	2138, 2100	38	2150, 2125	25

^{a} Measured in Nujol mull. ^{b} Cis stretch-stretch interaction. ^{c} Fumaronitrile. ^{d} Maleic anhydride.

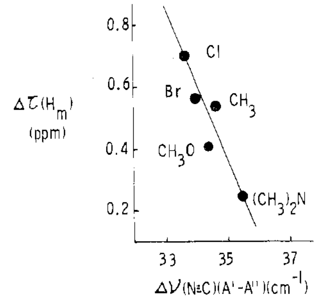

Figure 3. Relationship between $\Delta\tau$(H$_m$) and $\Delta\nu$(N≡C)(A′–A″).

nitrosobenzenes. The values of upfield shifts ($\Delta\tau$) of ring protons on complexation are also shown. Assignments of the ring proton signals of free nitrosobenzenes were made by evaluating the shielding constants of the NO group in acetone by use of the additivity law of substituent shielding constants so as to fit the observed chemical shifts. The shielding constants of para substituents (Me$_2$N, MeO, Me, Cl, Br) in acetone being unavailable, we employed the Varian's value for polar solvents.[30] The shielding constants of the N=O group thus obtained are −0.72 and −0.32 for ortho and meta protons, respectively. The assessed values are reasonable in view of the corresponding values found in cyclohexane[31] (ortho, −0.58; meta, −0.26). Similarly the shielding constants of the nitrosobis(*tert*-butyl isocyanide)nickel moiety $-\overline{\mathrm{N{-}O{-}Ni}}(t\text{-BuNC})_2$ were assessed to be 0.0 and 0.16 for ortho and meta protons, respectively, indicating the electron-donating nature of $-\overline{\mathrm{N{-}O{-}Ni}}(t\text{-BuNC})_2$. Thus a considerable electron drainage into nitrosobenzene from nickel is evident from the ir and ^{1}H NMR data (Figure 3).

Ligand Reactions. As a corollary of the above spectroscopic study we have expected facile N–O bond cleavage reactions of the coordinated nitrosobenzenes. This is borne out by several stoichiometric reactions as illustrated in Scheme I. Reaction of Ni(PhNO)(t-BuNC)$_2$ with 2 mol of PPh$_3$ at ambient temperature in benzene gives t-BuNCO (23%) and Ph$_3$PO (44%), together with Ni(PPh$_3$)$_2$(t-BuNC)$_2$[12] (19%). Although Ph$_3$PO might be derived from uncoordinated PhNO and PPh$_3$, complete dissociation of PhNO from Ni(PhNO)(t-BuNC)$_2$ is unlikely because of the formation of a substantial amount of t-BuNCO. A similar reaction with 4 mol of t-BuNC in benzene under reflux affords t-BuNCO (31%) and Ni(t-BuNC)$_4$ (13%). These reactions are then regarded as a typical oxygen atom transfer redox reaction.[12] An intramolecular phenylnitrene transfer to coordinated isocyanide is observed for a thermal reaction of Ni(PhNO)(t-BuNC)$_2$ in the presence of a small amount of H$_2$O at ambient temperature; PhNHCONH(t-Bu) (47% yield) undoubtedly resulted from hydration of the carbodiimide initially formed. Oxygenation of nitrosobenzene is effected at ambient temperature by use of Ni(PhNO)(t-BuNC)$_2$ to give Ni(PhNO$_2$)(t-BuNC)$_2$[12] together with azoxybenzene presumably derived by phenylnitrene transfer to nitrosobenzene.

The reaction with isocyanide can be carried out catalytically. Thus a mixture of PhNO and t-BuNC in benzene in the presence of a catalytic amount of Ni(t-BuNC)$_4$ was refluxed to produce t-BuNCO (30% based on PhNO) along with PhN=C=N(t-Bu), PhN=NPh, and (t-BuNH)$_2$CO. In the absence of Ni(t-BuNC)$_4$ the reaction of t-BuNC with PhNO under a similar condition produced *t*-BuNCO in 17% yield.

Compared to PhNO, PhNO$_2$ is less reactive for the reaction. Free PhNO$_2$ with *t*-BuNC at 130 °C gives only a trace of *t*-BuNCO (1%), while the Ni(*t*-BuNC)$_4$-catalyzed reaction of PhNO$_2$ gave 83% (based on *t*-BuNC) of *t*-BuNCO, together with PhN═C═N(*t*-Bu), PhN═NPh, and PhN═N(O)Ph. Using "Pd(*t*-BuNC)$_2$" as a catalyst, an exothermic reaction occurs with a similar result. The metal-catalyzed atom-transfer reaction takes place readily with electrophilic nitro compounds and the yield of *t*-BuNCO increases in the order *t*-BuNO$_2$ < *m*-Me$_2$NC$_6$H$_4$NO$_2$ < C$_6$H$_5$NO$_2$ < *m*-ClC$_6$H$_4$NO$_2$ < 3,5-Cl$_2$C$_6$H$_3$NO$_2$. A closely related reaction may be the formation of PhNCO and PhN═NPh from PhNO$_2$ and CO catalyzed by metal carbonyls.[32,33]

Experimental Section

^{1}H NMR spectra of the complexes and free nitrosobenzenes were measured in acetone-d_6 and acetone, respectively, by a 100-MHz Jeol Model JNM 4H-100 using TMS as internal reference. Ir spectra were recorded on a Hitachi Perkin-Elmer Model 225. The N≡C stretching frequencies were measured in benzene and calibrated against the bands of CO$_2$. All reactions and physical measurements were carried out under a pure nitrogen atmosphere. The following compounds were prepared according to the known methods: Ni(*t*-BuNC)$_{2\text{ or }4}$,[13] Pd(*t*-BuNC)$_2$,[13] M(CH$_2$═CH$_2$)(PPh$_3$)$_2$ (M = Ni,[14] Pd,[15] Pt[16]), PdL$_2$[17] [L = P(*t*-Bu)$_3$, PPh(*t*-Bu)$_2$)], *p*-XC$_6$H$_4$NO (X = Me$_2$N,[3] MeO,[34] Me,[35] H,[36] Cl,[34] Br[35]).

Preparation of M(ArNO)L$_2$. (a) Ni(PhNO)(*t*-BuNC)$_2$. Nitrosobenzene (140 mg, 1.3 mmol) was added to a suspension of Ni(*t*-BuNC)$_4$ (470 mg, 1.2 mmol) in *n*-hexane (10 ml) at −30 °C. The yellow color of Ni(*t*-BuNC)$_4$ gradually changed to red on warming of the compound to room temperature. After 4 h of stirring at ambient temperature, red microcrystals which formed were filtered, washed with *n*-hexane, and dried in vacuo (400 mg, 99%). Similarly Ni(*p*-XC$_6$H$_4$NO)(*t*-BuNC)$_2$ (X = Me$_2$N, MeO, Me, Cl, Br) and Ni(3,4-Cl$_2$C$_6$H$_3$NO)(*t*-BuNC)$_2$ were obtained quantitatively.

(b) Pd(*p*-ClC$_6$H$_4$NO)(*t*-BuNC)$_2$. A mixture of Pd(*t*-BuNC)$_2$ (136 mg, 0.5 mmol) and *p*-ClC$_6$H$_4$NO (72 mg, 0.5 mmol) in *n*-hexane (10 ml) was stirred at 0 °C for 10 h. Orange microcrystals which separated were filtered, washed with *n*-hexane, and dried in vacuo (180 mg, 87%).

(c) Pt(PhNO)(PPh$_3$)$_2$. To a suspension of Pt(CH$_2$═CH$_2$)(PPh$_3$)$_2$ (150 mg, 0.2 mmol) in *n*-hexane (10 ml) was added PhNO (20 mg, 0.2 mmol) at room temperature and the mixture was stirred for 2 h at ambient temperature to give a yellow powder (130 mg, 78%). Similar reactions of PhNO with M(CH$_2$═CH$_2$)(PPh$_3$)$_2$ (M = Ni, Pd) gave M(PhNO)(PPh$_3$)$_2$.

Preparation of Pd$_3$(PhNO)$_3$L$_3$ (L = PPh(*t*-Bu)$_2$, P(*t*-Bu)$_3$). A mixture of Pd[PPh(*t*-Bu)$_2$]$_2$ (285 mg, 0.5 mmol) and PhNO (55 mg, 0.5 mmol) in *n*-hexane (10 ml) was stirred at room temperature for 22 h. After filtration of amorphous precipitates, the red solution was concentrated in vacuo to give red crystals containing a trace of colorless crystals. The latter being removed by washing with MeOH, the red crystals were recrystallized from benzene–*n*-hexane to give Pd$_3$(PhNO)$_3$[PPh(*t*-Bu)$_2$]$_3$C$_6$H$_6$ (84 mg, 34%).

A similar reaction using Pd[P(*t*-Bu)$_3$]$_2$ (153 mg, 0.3 mmol) and PhNO (0.032 g, 0.3 mmol) gave Pd$_3$(PhNO)$_3$[P(*t*-Bu)$_3$]$_3$ (20 mg, 16%) as red crystals after recrystallization from hot *n*-hexane.

Preparation of Ni(PhNO$_2$)$_2$(*t*-BuNC)$_2$. To a suspension of Ni(*t*-BuNC)$_4$ (703 mg, 0.8 mmol) in *n*-hexane (20 ml) was added PhNO (428 mg, 4 mmol) at room temperature. After 30 min, the reddish brown precipitates were filtered, washed with *n*-hexane, and dried in vacuo. This was identified as Ni(PhNO$_2$)(*t*-BuNC)$_2$ by comparing its melting point and ir spectrum with those of the authentic sample prepared from Ni(*t*-BuNC)$_4$ and PhNO$_2$. The yield was almost quantitative. The above filtrate was concentrated and the residue was chromatographed on silica gel using a mixture of *n*-hexane and benzene to give azoxybenzene (117 mg, 30%).

Reaction of Ni(PhNO)(*t*-BuNC)$_2$. (a) With PPh$_3$. A mixture of Ni(PhNO)(*t*-BuNC)$_2$ (273 mg, 0.83 mmol) and PPh$_3$ (432 mg, 1.65 mmol) in benzene (15 ml) was stirred at ambient temperature for 10 h, and the mixture was distilled to give *t*-BuNCO (19 mg, 23%) and a dark brown oily residue. The residue was extracted with hot *n*-hexane (30 ml) and the extract was cooled to precipitate Ph$_3$PO. After filtration of this solid, the filtrate was concentrated to about 15 ml and cooled to give orange-yellow crystals together with further crops of Ph$_3$PO (total 110 mg, 43.5%). The orange-yellow crystals were recrystallized from *n*-hexane to give orange crystals of Ni(PPh$_3$)$_2$(*t*-BuNC)$_2$, mp 123–126 °C dec (116 mg, 18.7%).

(b) With *t*-BuNC. A mixture of Ni(PhNO)(*t*-BuNC)$_2$ (300 mg, 0.91 mmol) and *t*-BuNC (300 mg, 3.6 mmol) in benzene (10 ml) was heated under reflux for 3 h. The mixture was distilled in vacuo to isolate *t*-BuNCO (28.5 mg, 31.6%) leaving a reddish brown oily residue. The residue was extracted with *n*-hexane and upon concentration the extract gave Ni(*t*-BuNC)$_4$ (45 mg, 13%).

(c) With H$_2$O. A mixture of Ni(PhNO)(*t*-BuNC)$_2$ (208 mg, 0.62 mmol) and H$_2$O (0.5 ml) in ether (15 ml) was stirred at room temperature for 4 h. After filtration of brown amorphous solids, the filtrate was concentrated to give colorless crystals of PhNHCONH(*t*-Bu), mp 168–171 °C (51 mg, 47%). The ir spectrum (cm^{-1}) showing ν(NH) (3280) and ν(CO) (1650) is identical with that of an authentic sample prepared from PhNCO and *t*-BuNH$_2$.

Reaction of PhNO and *t*-BuNC. A mixture of PhNO (1.00 g, 9.3 mmol), *t*-BuNC (1.0 mg, 9.4 mmol), and Ni(*t*-BuNC)$_4$ (0.05 g, 0.13 mmol) in benzene (15 ml) was heated under reflux for 5 h. The mixture was distilled at 25 °C (10 mmHg) to give *t*-BuNCO (280 mg, 30%) leaving a brown oily residue. The residue was chromatographed on silica gel and eluted with *n*-hexane. Evaporation of the yellow eluate left a yellow oil, which on cooling gave an orange solid of PhN═NPh (5 mg, 0.5%). After filtration, the yellow-orange filtrate was distilled to give PhN═C═N(*t*-Bu) as a pale yellow oil (81 mg, 5%), bp 70–75 °C (3 mmHg). Anal. Calcd for C$_{11}$H$_{14}$N$_2$: C, 75.83; H, 8.09; N, 16.07. Found: C, 74.84; H, 7.91; N, 15.90. Ir spectrum (cm^{-1}): ν(N═C═N) 2100. ^{1}H NMR spectrum (τ, in CCl$_4$): 8.60 (*t*-Bu), 2.87 (C$_6$H$_5$). These spectral data were completely identical with those of an authentic sample of the carbodiimide prepared from PhNHCSNH(*t*-Bu) and HgO. Elution with *n*-hexane–benzene gave PhN═N(O)Ph (270 mg, 14%). Further elution with MeOH gave (*t*-BuNH)$_2$CO (60 mg, 7.5%). In the absence of Ni(*t*-BuNC)$_4$ the reaction of PhNO and *t*-BuNC under a similar condition gave *t*-BuNCO (17%) and PhN═N(O)Ph (8%). The yields of *t*-BuNCO, PhN═C═N(*t*-Bu), and (*t*-BuNH)$_2$CO were based on *t*-BuNC while those of PhN═NPh and PhN═N(O)Ph were based on PhNO.

Reaction of PhNO$_2$ and *t*-BuNC. A mixture of *t*-BuNC (8.3 g, 100 mmol), PhNO$_2$ (9.8 g, 80 mmol), and Ni(*t*-BuNC)$_4$ (0.39 g, 1 mmol) was heated at 130 °C for 12 h. The reaction mixture was distilled in vacuo to give *t*-BuNCO (8.2 g, 82.8%), PhN═C═N(*t*-Bu) (1.1 g, 6.6%), and unreacted PhNO$_2$ (1.0 g, 10.2%). The distillation residue was chromatographed on silica gel and eluted with *n*-hexane–benzene affording PhN═NPh (2.9 g, 40.0%) and PhN═N(O)Ph (3.1 g, 40.7%). Subsequent elution with a mixture of ether–benzene gave PhNHCONH(*t*-Bu) (1.2 g, 6.3%), a hydration product of PhN═C═N(*t*-Bu). The yields of *t*-BuNCO, PhN═C═N(*t*-Bu), and PhNHCONH(*t*-Bu) were based on *t*-BuNC while those of other products were based on PhNO$_2$. In the absence of N(*t*-BuNC)$_4$, the reaction gave *t*-BuNCO as a sole product in an extremely low yield (1%). Similarly several nitro compounds RNO$_2$ (10 mmol) were allowed to react with *t*-BuNC (30 mmol) in the presence of Ni(*t*-BuNC)$_4$ (0.3 mmol) at 80 °C for 4 h. The yields (%) of *t*-BuNCO shown in parentheses are for R = *t*-Bu (0.27), *m*-Me$_2$NC$_6$H$_4$ (1.16), C$_6$H$_5$ (2.95), *m*-NCC$_6$H$_4$ (9.93), and 3,4-Cl$_2$C$_6$H$_3$ (16.32).

Registry No. Ni(3,4-Cl$_2$C$_6$H$_3$NO)(*t*-BuNC)$_2$, 57718-86-2; Ni(*p*-ClC$_6$H$_4$NO)(*t*-BuNC)$_2$, 57718-87-3; Ni(*p*-BrC$_6$H$_4$NO)(*t*-BuNC)$_2$, 57718-88-4; Ni(PhNO)(*t*-BuNC)$_2$, 57718-89-5; Ni(*p*-MeC$_6$H$_4$NO)(*t*-BuNC)$_2$, 57718-90-8; Ni(*p*-MeOC$_6$H$_4$NO)(*t*-BuNC)$_2$, 57718-91-9; Ni(*p*-Me$_2$NC$_6$H$_4$NO)(*t*-BuNC)$_2$, 57761-86-1; Pd(*p*-ClC$_6$H$_4$NO)(*t*-BuNC)$_2$, 57718-92-0; Ni(PhNO)(PPh$_3$)$_2$, 57718-93-1; Pd(PhNO)(PPh$_3$)$_2$, 57718-94-2; Pt(PhNO)(PPh$_3$)$_2$, 57718-95-3; Pd$_3$(PhNO)$_3$[P(*t*-Bu)$_3$]$_3$, 54374-33-3; Pd$_3$(PhNO)$_3$[PPh(*t*-Bu)$_2$]$_3$, 57718-96-4; Ni(*t*-BuNC)$_4$, 19068-11-2; Pd(*t*-BuNC)$_2$, 24859-25-4; Pt(CH$_2$═CH$_2$)(PPh$_3$)$_2$, 12120-15-9; Pd[PPh(*t*-Bu)$_2$]$_2$, 52359-17-8; Pd[P(*t*-Bu)$_3$]$_2$, 53199-31-8; PPh$_3$, 603-35-0; *t*-BuNC, 7188-38-7; PhNO, 586-96-9; PhN═C═N(*t*-Bu), 2219-34-3; PhNO$_2$, 98-95-3; *t*-BuNCO, 1609-86-5.

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Macrocyclic Nickel(II) Complexes with New, Dimethyl-Substituted 13- and 14-Membered Tetraaza Ligands

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Catalytic reduction of the diimine linkages of 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-11,13-dienenickel(II) hexafluorophosphate, $[Ni([13]dieneN_4)](PF_6)_2$, and 12,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-12,14-dienenickel(II) hexafluorophosphate, $[Ni([14]dieneN_4)](PF_6)_2$, in aqueous solution over Raney nickel yields Ni(II) complexes containing the fully reduced, dimethyl-substituted macrocyclic ligands. Conversion of the PF_6^- salts to NO_3^- derivatives has been accomplished by column chromatography. Compounds with a variety of other anions have been prepared by metathetical reactions on solutions of the NO_3^- complexes. Ten new complexes have been characterized on the basis of elemental analyses, conductivity and magnetic susceptibility measurements, and infrared and electronic spectral studies. $[Ni([13]aneN_4)]X_2$ and $[Ni([14]aneN_4)]X_2$ where $X^- = PF_6^-$ and I^- contain singlet ground-state Ni(II) and the planar forms of both macrocyclic ligands. Axial coordination occurs when $X^- = Cl^-$, Br^-, and NO_3^- and complexes of formulation $[Ni([14]aneN_4)X_2]$ have been characterized as high spin tetragonal. Two complexes, $[Ni_2([13]aneN_4)_2ox](PF_6)_2$ and $[Ni_2([14]aneN_4)_2ox](PF_6)_2$, are dimers which contain oxalato bridging groups. These two compounds, along with monomeric $[Ni([14]aneN_4)(SCN)_2]$, exhibit pseudooctahedral Ni(II) spectral characteristics and must contain folded forms of the macrocyclic ligands. Analysis of electronic spectral data for the tetragonal complexes gives a Dq^{xy} of 1470 cm^{-1} for the dimethyl-substituted 14-membered ligand. This value is nearly the same as that reported for cyclam which leads us to conclude that substitution of two methyl groups on the cyclam ring has negligible steric and electronic effects.

Introduction

Concentrated efforts in several research laboratories over the past 15 years have brought a new degree of sophistication to studies of macrocyclic metal complexes.[1-5] While the earlier work centered almost exclusively on development of new and sometimes novel methods for synthesis of a broad range of seemingly unrelated ligands and complexes, recent studies have involved application of synthetic expertise to the design of new series of compounds which possess specific structural characteristics.[6-10] Structural parameters which can be varied almost at will include the nature and oxidation state of the metal ion, anion, ring size and charge, donor atoms, degree of unsaturation, and type of substituents on the rings. Further work has shown that cause and effect relationships exist between the chemical reactivity of the metal ion and the structural and electronic properties of the complex.[5,11]

The synthetic studies derive added significance when the new compounds can be used as models for natural products; e.g., complexes with tetraaza macrocyclic ligands can be designed to have many characteristics in common with metalloporphyrins, vitamin B_{12}, and chlorophyll. Special types of chemical reactivity can sometimes be induced by elegant complex design; e.g., sterically hindered iron(II) porphyrins combine reversibly with molecular oxygen under relatively mild conditions and thus serve as models for myoglobin.[12-15]

Recent physical studies on selected macrocyclic complexes have involved measurement of thermodynamic and kinetic stabilities and correlation of differences with specific structural features.[16-19] Such studies when performed on model complexes are valuable in that they provide a means of evaluating the importance of specific factors which may affect biological activity. For example, it is well known that most macrocyclic ligands in aqueous solution form more stable complexes with metal ions than open-chain ligands with the same donor groups.[3,17,18] Rather extensive investigation of the thermodynamics and kinetics of complexation of selected metal ions with tetraaza macrocyclic ligands has revealed that the differences are due not only to cyclization but also to (1) steric effects which arise from substitution on the alkyl backbone or nitrogen donor atoms of the ring, and (2) differences in reactivity of secondary vs. tertiary nitrogen donor atoms. The importance of steric effects has been demonstrated recently for Ni(II) and Cu(II) complexes with ligands I–IV.[18,19] The ligands are identified as 1,4,8,11-tetraazacyclotetradecane (cyclam), I; *meso*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane (5,12-Me_2cyclam), II; *meso*-5,7,7,12,-14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (tet-*a*), III; and *rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-