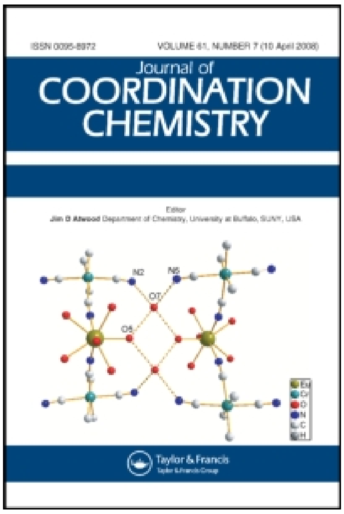

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NO STRETCHING FREQUENCY AS A FUNCTION OF LIGAND BASICITY IN [NI (NO) (PHOSPHITE)$_3$] BF$_4$ COMPLEXES

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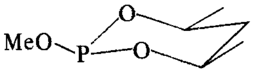
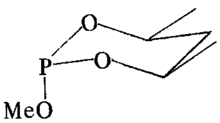
In a recent paper we reported the first example of phosphite complexes of the type $[Ni(NO)L_3]^+(L{=}P(OCH_2)_3CMe)$.[1]. In the present paper we report further examples of these cations wherein L = **1**–**8** and **10**.

$P(O{-}n{-}Pr)_3$ (1) $P(OEt)_3$ (2)

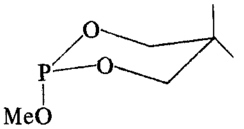
$P(OMe)_3$ (3)



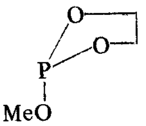
(4)



(5)

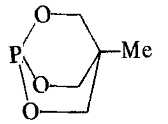


(6)

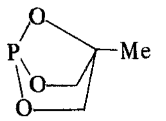


(7)

$P(OPh)_3$ (8)



(9)



(10)

In previous publications from these laboratories we have shown that the Lewis basicity of the phosphorus lone pair in phosphites decreases when molecular constraint is increased.[2]

$$\mathbf{3} > \mathbf{6} > \mathbf{7} > \mathbf{9} > \mathbf{10}$$

Thus for example, the order of basicities toward a proton, a borane group and an oxygen atom has been observed spectroscopically and electronic effects accounting for these results have been discussed.[2a,3] Similar studies with **4** and **5** lead to the order

$$\mathbf{4} > \mathbf{5}$$

which has been rationalized in terms of orbital symmetries.[2a,3] It was therefore of interest to evaluate the influence of these geometrically based variations in basicity on ν(NO) in the above nickel complexes.

EXPERIMENTAL

All solvents were reagent grade and were purged with prepurified nitrogen before use. $NOBF_4$ from Aldrich Chemical Company was used without further purification.

Infrared spectra of CH_2Cl_2 solutions were obtained with a Beckman IR-4250 instrument using sodium chloride optics. High resolution mass spectra were run on an AEI MS902 mass spectrometer. Phosphorous-31 nmr spectra were recorded on a Bruker HX-90 spectrometer operating in the Fourier transform mode. Routine ^1H nmr spectra were obtained on either a Varian Associates A-60 or a Hitachi Perkin-Elmer R20-B nmr spectrometer.

The ligands $P(OEt)_3$, $P(OMe)_3$ and $P(OPh)_3$ were obtained commercially while $P(O{-}n{-}Pr)_3$ was prepared as follows. To 112 ml (1.50 mol) of n–PrOH was slowly added under a flow of nitrogen, 43.6 ml (0.500 mol) of PCl_3 while the reaction mixture was kept at room temperature with a cold water bath. The product possessing the expected pnmr spectrum distilled at 50–51° at 0.1 torr. The cyclic ligands **4**[4], **5**[5], **6**[5], **7**[6], **9**[7] and **10**[3c] were prepared by methods described previously.

The complexes $Ni(1)_4$[8], $Ni(2)_4$[8], $Ni(4)_4$[9], $Ni(5)_4$[9], $Ni(6)_4$[10] and $Ni(10)_4$[11] were prepared following methods described elsewhere. The complex $Ni(\mathbf{9})_4$ was made by reduction of the corresponding $\{NiL_5\}(BF_4)_2$ salt[12] in the presence of $NaHCO_3$[13]

Ni(3)$_4$

Although the preparation of this complex has been reported before,[14] the following procedure carried

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†Author to whom correspondence should be addressed.

out under prepurified nitrogen was found to be convenient. Into 20 ml of 95% EtOH was dissolved 1.5 g (6.3 m mol) of $NiCl_2 \cdot 6H_2O$. After cooling the solution to 0°, 3.7 ml (3.15 m mol) of **3** was added, which turned the green color to a dark red. Upon adding 1.5 ml (14.5 m mol) of $HNEt_2$, the solution turned to a light green. The product precipitated as a fine powder on adding 60 ml of deoxygenated water. After extraction of the product with 20 ml of hexane, the solvent was evaporated under vacuum leaving a white paste which was then dehydrated with 5 ml of 2,2-dimethoxypropane. Pumping to dryness under vacuum left the product as a white air-sensitive powder.

Ni(7)₄

This new complex was prepared after the manner of Vinal and Reynolds[8] and the white powdery product exhibited a parent peak in the mass spectrum at 545.9910 in agreement with the calculated value of 545.9884.

Ni(8)₄

Although this complex has been made by carbonyl substitution of $Ni(CO)_4$ and by reduction of a nickel(II) salt in the presence of excess ligand,[14] we find the following preparation quite efficient. In 10 ml of degassed CH_2Cl_2 was dissolved 3.5 g (11 m mol) of ligand under nitrogen. To this solution was added 0.44 g (2.7 m mol) of $Ni(CH_2CHCN)_2$[15] and the reaction mixture was allowed to stir for 45 min. After removal of the solvent under vacuum, the cream colored paste was dissolved in benzene. After filtration, the complex was precipitated by addition of MeOH and cooling to 0°. The yield and ^{31}P nmr shift in d_6-benzene (−129.8 ppm relative to external 85% H_3PO_4) agrees well with previously reported values of −128.8[16] and −130.3[17] ppm.

{Ni(NO)L₃}BF₄

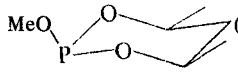
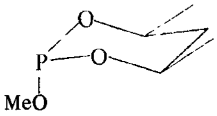
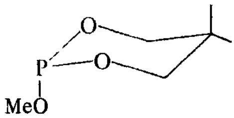
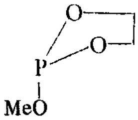
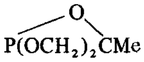
One millimole of the NiL_4 complex was dissolved in degassed CH_2Cl_2 in a nitrogen atmosphere. To this was added with vigorous stirring 0.11 g (1.0 m mol) of $NOBF_4$. After stirring the solution for 10 min., a portion was transferred to an ir cell and the spectrum recorded.

DISCUSSION

All of the NiL_4 complexes, except for those containing acyclic ligands, tolerated brief exposure to air without showing signs of decomposition.

TABLE I

$\nu(NO)$ values for $Ni(NO)L_3^+$ complexes and $^1J(PH)$ paramete for the corresponding HL^+ species

L		$\nu(NO)$ (cm^{-1})	$^1J(PH)^a$ (Hz)
$P(O{-}n{-}Pr)_3$	(*1*)	1818	$-^c$
$P(OEt)_3$	(*2*)	1819	811^d
$P(OMe)_3$	(*3*)	1824	826.2
	(*4*)	1830	850.6
	(*5*)	1836	865.0
	(*6*)	1841	861.2
	(*7*)	1853	890.4^e
$P(OPh)_3$	(*8*)	1866	875^d
$P(OCH_2)_3CMe$	(*9*)	1871^b	899.2
 $P(OCH_2)_2CMe$	(*10*)	1897	928.8

[a] Value taken from ref. 3b unless noted otherwise.
[b] Compares favorably with 1872 cm^{-1} reported in ref. 1.
[c] Not reported.
[d] G. A. Olah and C. W. McFarland, *J. Org. Chem.*, 36, 1374 (1971).
[e] Because compound 7 is unstable in strongly acid media, the methyl derivative $MeOP(OCH_2CHMeO)$ was used for this measurement.[3b]

The NO stretching frequencies listed in Table I increase markedly from ligand **1** to **10**, generally paralleling the rise in $^1J(PH)$ in HL^+.[3c]. A plot of these two parameters in Figure 1 reveals a correlation coefficient of 0.95 suggesting that the origin of the two trends is the same. Decreasing sigma basicity accounts for the rise in $^1J(PH)$ since increasing phosphorus lone pair s character and phosphorus positive charge contribute to the rise in this one-bond coupling. Since reduced phosphorus lone pair availability allows greater electron drift from the antibonding pi MO's in the NO ligand onto the metal, $\nu(NO)$ is expected to rise. The increased ligand pi acidity upon ligand constraint[2b] merely augments the effect on ν(NO).

It seems reasonable to suppose then, that any frequency dominated by the electron inductive effect of a phosphorus ligand should correlate well with the corresponding ^{1}JPH values. Thus, for example, Tolman[18] concluded from a correlation of substituent parameters with Kabachnik's σ parameter that the frequency for the A_1 mode in the Ni(CO)$_3$L complexes (L = **2**, **3**, **8**, **9** and PhOP(OCH$_2$)$_2$) reflected an increasing electron acceptor power of the ligands. The correlation coefficient of 0.93 for a plot of these CO frequencies versus ^{1}J(PH) (Table II) supports this hypothesis very well. Table II also

TABLE II

Correlation of ^{1}J(PH) *versus* CO and NO infrared modes in metal complexes containing phosphorus ligands

Complex	ν(CO) mode[a] [No. of points]	Corr. Coeff.	Equation $y = mx + b$		References
			m	b	
Cr(CO)$_5$L	A_1^1 [9]	0.82	0.0927	1894	20, 21, 22, 23, 28, 34, 35
	A_1^2 [10]	0.89	0.0400	2043	
	[9]	0.92	0.0360	2045	
Mo(CO)$_5$L	A_1^1 [12]	0.82	0.0958	1902	20, 21, 22, 24, 34, 35, 37, 44
	[11]	0.83	0.1022	1898	
	A_1^2 [13]	0.43	0.0214	2060	
	[12]	0.74	0.0315	2055	
	[11]	0.79	0.0253	2058	
W(CO)$_5$L	A_1^1 [14]	0.85	0.0915	1895	20, 21, 22, 23, 25, 34, 41
	[13]	0.94	0.0455	2045	
	E_1 [14]	0.93	0.0610	1907	
Fe(CO)$_4$L	A_1^1 [10]	0.76	0.0699	1938	20, 21, 22, 30, 34, 40, 47
	[9]	0.89	0.0667	1939	
	A_1^2 [10]	0.89	0.0752	2003	
	[9]	0.91	0.0741	2004	
cis-Cr(CO)$_4$L$_2$	A_1^1 [8]	0.92	0.1059	1855	22, 23, 26, 28, 30, 31, 35, 39, 44
	A_1^2 [9]	0.91	0.0966	1954	
cis-Mo(CO)$_4$L$_2$	A_1^1 [16]	0.87	0.1264	1854	26, 27, 28, 31, 34, 39, 44, 45, 46
	[15]	0.90	0.1189	1858	
	A_1^2 [16]	0.92	0.0918	1971	
	[15]	0.93	0.0880	1973	
cis-W(CO)$_4$L$_2$	A_1^1 [7]	0.88	0.1247	1837	26, 29, 31, 38, 44
	A_1^2 [7]	0.95	0.0959	1960	
trans-Mo(CO)$_4$L$_2$	E_u [9]	0.95	0.1114	1825	26, 28, 35, 37, 44
	B_{1g}[5]	0.96	0.1841	1816	
trans-Mo(CO)$_4$L$_2$	E_u [8]	0.68	0.0723	1860	24, 26, 37, 44
	[7]	0.95	0.1068	1841	
trans-Fe(CO)$_3$L$_2$	E [8]	0.94	0.1743	1783	20, 21, 30, 34, 40, 47
Ni(CO)$_3$L	A_1 [14]	0.93	0.0591	2036	18, 19, 20, 21, 32
Ni(CO)$_2$L$_2$	A_1 [13]	0.91	0.1328	1937	19, 20, 21, 30, 32, 33, 34, 36
Ni(CO)L$_3$	A_1 [10]	0.87	0.2204	1808	20, 21, 30, 32, 33, 34, 36
	[9]	0.93	0.2081	1813	
[Ni(NO)L$_3$]$^{+1}$	$A_1^{(NO)}$[9]	0.94	0.6612	1275	1, This work
Co(NO)(CO)$_2$L	A_1 [6]	0.98	0.0673	2001	42, 43
	B_1 [6]	0.98	0.0814	1934	
	$A_1^{(NO)}$ [6]	0.96	0.0922	1697	

[a] Unless stated otherwise.

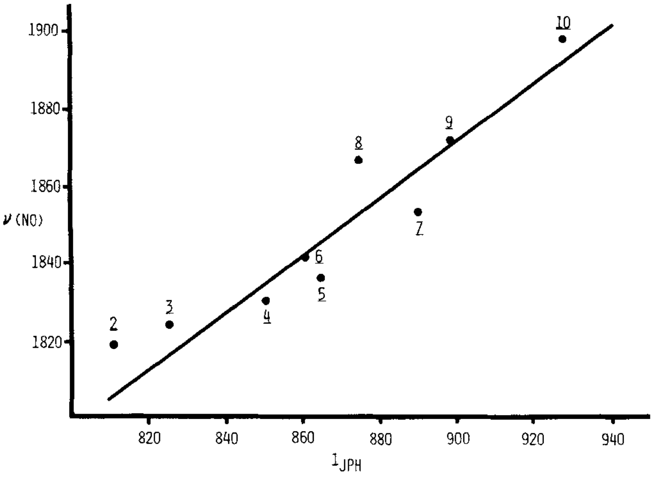


FIGURE 1 Plot of ν(NO) for a series of $\{Ni(NO)L_3\}BF_4$ complexes (L = 2 – 10) *versus* $^1J(PH)$ for the corresponding HL^+ species.

contains correlation coefficients for similar plots obtained from information in the literature for a variety of other complexes. In addition to points for phosphines and phosphites, almost half of the plots include a point for PF_3 which about doubles the range of each plotted parameter. Thus the correlations for $W(CO)_5L$, cis-$Mo(CO)_4L_2$, $Ni(CO)_3L$, $Ni(CO)L_3$ and $Co(NO)(CO)_2L$ (which in all cases are quite respectable) are probably the most reliable since they encompass the maximum range of phosphorus ligand electronegativities. While these results do not negate the possibility of dative pi bonding in metal-phosphorus complexes, it can be concluded that CO and NO stretching frequencies do reflect changes in the sigma donor characteristics (i.e. lone pair s character and nuclear charge) which determine the magnitude of $^1J(PH)$.

Interestingly, where the number of points was reduced by one in order to gauge the improvement in the correlation coefficient (which in several cases was considerable) the ligand involved in the majority of instances was PCl_3. The reason for the apparent anomalous behavior of this ligand is not presently clear.

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