An Azobenzene Complex of Nickel(0): Comparison of Azobenzene with Olefinic Ligand in $d\pi$ Acceptor Properties

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Summary Preparation and spectroscopic data of M(L)$(Bu^tNC)_2$, (L = azobenzene or olefins), are described with particular emphasis on the $d\pi$-acceptor properties of azobenzene.

IT seemed of interest to examine the $d\pi$-acceptor properties of an a N=N linkage in, *e.g.*, azobenzene. However, no relevant mononuclear complex was available, in which an azo-compound was involved in delocalised bonding to a metal[1,2] as in olefin–metal complexes. We have found a simple route to mononuclear nickel complexes Ni(L)$(Bu^tNC)_2$, and their i.r. NC stretching bands provide information on the relative π-acidity of the ligands, L.

An equimolar mixture of "Ni $(Bu^tNC)_2$"[3] and azobenzene in ether was stirred under nitrogen at ambient temperature, affording orange-red crystals (dec. 163—164°) of Ni(PhN=NPh) $(Bu^tNC)_2$.† Similarly, Ni(L)$(Bu^tNC)_2$ were prepared for L = oxygen,[3] tetracyanoethylene (TCNE),[3] fumaronitrile (FN), maleic anhydride (MA) and tolane. Their i.r. and ^1H n.m.r. data are summarised in the Table.

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† The elemental analysis agreed reasonably with the theoretical values.

I.r. and n.m.r. spectra of Ni(L)(Bu^{t}NC)$_2$

	I.r. (cm^{-1})[a]		N.m.r. (p.p.m.)[b]	
	ν (N≡C)	other	τ (Bu^t)	τ (olefin)
Ni (O$_2$) (Bu^{t}NC)$_2$	2196, 2178	————	8·59[c]	————
Ni(TCNE)(Bu^{t}NC)$_2$	2194, 2179	ν (C≡N) 2222, 2219	9·08	————
Ni (PhN=NPh) (Bu^{t}NC)$_2$	2168, 2140	δ (C—H) 756, 690	8·51 (9)[d]	2·80 (3)[d,e] 3·15 (2)[d,e]
Ni (FN)(Bu^{t}NC)$_2$	2162, 2138	ν (C≡N) 2199	9·12 (9)	7·55 (1)
Ni (MA)(Bu^{t}NC)^2	2159, 2118	ν (C=O) 1799, 1730	9·08 (9)	6·19 (1)
Ni (PhC≡CPh)(Bu^{t}NC)$_2$	2138, 2100	ν (C≡C) 1810 δ (C–H) 762, 693	8·47 (9)[d]	2·35 (2)[d,e] 2·71 (3)[d,e]

[a] Measured in Nujol mull.

[b] Measured in benzene unless otherwise stated, using Me$_4$Si as internal reference. Both t-butyl and olefinic protons were observed as sharp singlets. Values in parentheses show relative intensities.

[c] Measured in CDCl$_3$

[d] Measured in (CD$_3$)$_2$CO.

[e] Aromatic protons, complex multiplets.

The azobenzene complex is diamagnetic and extremely air-sensitive. The spectroscopic data (Table) suggest side-on co-ordination of the azo-group and the absence of a σ-metal–aromatic carbon bond. This latter type of co-ordination may only be found in (π-C$_5$H$_5$)Mo(PhN=NPh).[4]

The two bands in the 2100—2196 cm^{-1} region observed for all these complexes are ascribable to the NC stretching absorptions (*a* and *b* modes) of the isocyanide ligands. There is an approximately linear correlation between the frequency of the *a* or *b* modes and the electron affinity of the ligand L, except for the tolane complex. Some caution is necessary, however, in inferring the π-acidity from the known or estimated electron affinities. For one thing, apart from the π_u orbitals, the ligands O$_2$ or acetylene will interact with metal orbitals with their two orthogonal π_g orbitals, whereas the other simple olefins interact *via* one π_g orbital. Also the bonding scheme for a metal–side-on azo-compound involving lone-pair orbitals will not be identical with that for olefin co-ordination Even with these reservations, the Table clearly indicates that azobenzene can act as a fairly strong π-acid.

The molecular structure of Ni(TCNE)(Bu^{t}NC)$_2$ may be described as a twisted planar structure (C_2) with a dihedral angle of 23°.[5] At present, no *X*-ray diffraction data are available for the other complexes, but we expect that the molecular structure of the azobenzene complex should resemble that of the FN or MA complexes and would not differ much from that of the TCNE complex.

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