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Preliminary communication

A new series of tautomeric complexes containing nickel–cobalt bonds, $(\pi\text{-}C_5H_5)NiCo(CO)_4L$ (L = tertiary phosphine or arsine).

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Although the isoelectronic compounds $[(\pi\text{-}C_5H_5)Ni(CO)]_2$[1] and $Co_2(CO)_8$[2] are known, the mixed metal complex $(\pi\text{-}C_5H_5)NiCo(CO)_5$ has not been reported. As a possible route to derivatives of this compound we examined the reaction of the $(\pi\text{-}C_5H_5)Ni(L)X$ complexes (L = tertiary phosphine or arsine; X = Cl or Br)[3] with $Na[Co(CO)_4]$ in tetrahydrofuran solution at room temperature. This proved successful, and has been found to give the brown $(\pi\text{-}C_5H_5)NiCo(CO)_4L$ or $(\pi\text{-}MeC_5H_5)NiCo(CO)_4L$ compounds. These are more or less unstable; when L is volatile, *e.g.* Me_3As or Et_3P, they decompose in the solid state, and all are unstable in solution.

Infrared spectral studies show that the new compounds contain both bridging and terminal carbonyl ligands. Thus it appears they have structures which are intermediate between those of $[(\pi\text{-}C_5H_5)Ni(CO)]_2$[4] and $Co_2(CO)_8$[5] which, in the solid state, contain $M(CO_\mu)_2M$ moieties. If it is assumed that the effective atomic number rule is obeyed, the most reasonable structures are those of the type $(\pi\text{-}C_5H_5)Ni(CO_\mu)_2Co(CO)_2L$ with a non-planar bridging system and a Ni–Co bond. Thus the ligand L must have migrated from the nickel to the cobalt atom during the displacement of X^- by $[Co(CO)_4]^-$. This is an unusual reaction, and its only precedent is in the displacement of CO from $[trans\text{-}(Ph_3P)_2Co(CO)_3]^+$ by $[Co(CO)_4]^-$ where a Ph_3P ligand migrates from one cobalt atom to the other[6].

A close inspection of the infrared spectra of the $(\pi\text{-}C_5H_5)NiCo(CO)_4L$ complexes and their methylcyclopentadienyl counterparts shows that in many instances the absorption bands due to their $\nu(CO)$ vibrations are extremely broad, even in hexane solution, and have irregular profiles. The spectra of $(\pi\text{-}C_5H_5)NiCo(CO)_4PPh_3$ and $(\pi\text{-}C_5H_5)NiCo(CO)_4P(C_6H_4F\text{-}p)_3$ (Table 1) are of this type. The relative intensities of these absorption bands change with both temperature and solvent, and so do their shapes. The $\nu(CO)$ absorption bands of $(\pi\text{-}C_5H_5)NiCo(CO)_4PCy_2Ph$ are narrow and well-resolved, but there are more of them than would be expected (Table 1) and their relative intensities vary with temperature. Furthermore, a decline in the importance of the absorption bands due to bridging carbonyl groups may be correlated with an increase in

TABLE 1

THE INFRARED SPECTRA OF SOME (π-C_5H_5)NiCo$(CO)_4$L COMPLEXES IN HEXANE SOLUTION
(peak positions (cm^{-1}) with relative peak heights in parentheses)

L	*Absorption bands*									
PCy_2Ph^a	1820(10)	1832(3.1)	1854(3.7)	1857(sh)	1915(0.8)	1941(1.0)	1975(5.1)	1984(15.2)	2025(6.3)	2031(11.5)
PPh_3	1830(10)		1861(5.0)		1925(4.3)	1946(4.5)	1984(13.3)		2029(16.0)	
$P(C_6H_4F\text{-}p)_3$	1830(10)		1864(5.1)		1924(5.6)	1949(5.7)	1986(15.6)		2030(23.6)	

^{a}Cy = cyclohexyl

the intensities of others which lie above 1900 cm^{-1} (*cf.* the spectra of (π-C_5H_5)NiCo$(CO)_4PPh_3$ and (π-C_5H_5)NiCo$(CO)_4P(C_6H_4F$-*p*$)_3$, Table 1).

These observations suggest that many of the observed absorption bands have more than one component, and that the compounds exist as mixtures of carbonyl bridged and non-bridged species in solution *cf.* $Co_2(CO)_8$[7] and its $[(LCo(CO)_3]_2$ derivatives[8,9]. This is being investigated at present.

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