Formation of Metal–Metal Bonds between Transition Metals *via* Lewis Acid–Base Interaction

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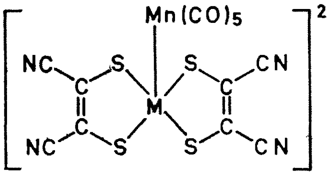
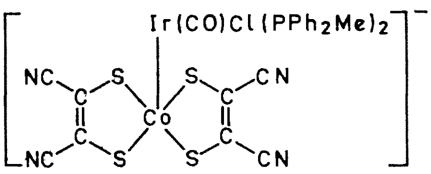
Summary Transition metal Lewis bases have been added to electrophilic iron and cobalt dithiolate systems yielding Lewis acid–base complexes containing labile metal–metal bonds.

WE report the synthesis and characterization of several novel Lewis acid–base complexes containing metal–metal bonds. It is well known[1,2] that the iron and cobalt maleonitrile-dithiolate (mnt) systems, $M(mnt)_2^-$, readily form monomeric five-co-ordinate adducts with typical Lewis bases such as phosphines. We have synthesized several five-co-ordinate adducts using $Mn(CO)_5^-$ and $Ir(CO)Cl(PPh_2Me)_2$ as the Lewis base and $M(mnt)_2^-$ (M = Co, Fe) as the Lewis acid. These compounds display several novel characteristics which we discuss.



(I) M = Co
(II) M = Fe



(III)

The tetra-alkylammonium salts of $[M(mnt)_2]_2^{2-}$ (M = Co, Fe) were prepared by published methods.[3] $NaMn(CO)_5$ was prepared in tetrahydrofuran by literature methods[4] and converted into the tetrabutylammonium salt. For the synthesis of (I) and (II) a 10% excess of a tetrahydrofuran solution of $(Bu_4N)Mn(CO)_5$ was added to $(Bu_4N)_2[M(mnt)_2]_2$ in tetrahydrofuran. The solvent was removed *in vacuo* and the residue was recrystallized from chloroform–ethanol. $Ir(CO)Cl(PPh_2Me)_2$ was synthesized according to the method of Collman and Kang.[5] Compound (III) was prepared by the addition of $(Me_4N)_2[Co(mnt)_2]_2$ to a solution of $Ir(CO)Cl(PPh_2Me)_2$ in CH_2Cl_2. After two minutes of being stirred at room temperature the remaining unreacted and insoluble starting material was removed by filtration and the filtrate was added to a silica-gel column under N_2. The column was eluted with acetone yielding a red-brown solution from which (III) was deposited on addition of pentane. Elution with CH_2Cl_2 gives a green solution which upon addition of pentane gives a compound which appears to be 2 : 1 complex containing an Ir–Co–Ir linkage. Physical properties of the compounds are given in the Table. The compounds are moderately stable in acetone, only slight decomposition occurring after 1 hr. The molar conductivities are consistent with the suggested structures.[2] Compounds (I) and (III) are diamagnetic but (I) becomes distinctly paramagnetic when exposed to air in the solid state for a few days.

An unusual feature of these compounds is the ease with which the M^1–M^2 bond is formed and cleaved.[6] Formation of M^1–M^2 bonds *via* Lewis acid–base interactions is quite uncommon.[7] Addition of various Lewis bases to acetone solutions of (I), (II), and (III) produces instant spectral changes suggesting rapid cleavage of the M^1–M^2 bond. The Mn hyperfine splitting in the e.s.r. spectrum of (II) (acetone solution) instantly collapses to the reported[3] doublet due to ^{31}P when tributylphosphine is added. This shows that the Fe–Mn bond is cleaved as the tributylphosphine adduct of $Fe(mnt)_2^-$ is formed.

We are attempting to extend the series of compounds reported above and are investigating their properties including e.s.r., electrochemical, and kinetic behaviour.[8]

TABLE

Compound[a]	U.v., visible (acetone) nm(log ε)	I.r. cm⁻¹ (KBr) ν(CN)	ν(CO)	Molar conductivity[b]
(I)[c]	499(3·6), 460(3·5sh) 415(3·6), 347(4·3)	2210(m) 2190(s)	2000(s) 1918(s) 1906(s)	288
(II)[c]	509(3·6), 349(4·4)	2210(m) 2190(s)	2000(s) 1922(s) 1906(s)	272
(III)[d]	500(3·3sh), 383(3·9)	2198(s)	2050(s)	144

[a] Satisfactory analytical data obtained for all compounds listed.
[b] Units are $cm^2 mol^{-1} ohm^{-1}$; 10^{-4} M-solution in acetone.
[c] Cation is tetrabutylammonium.
[d] Cation is tetramethylammonium.

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