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Preliminary communication

Metallocene analogues containing poly-1-pyrazolylborate or poly-1-pyrazolylmethane ligands and fully conjugated carbocyclic π-acceptor ligands

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SUMMARY

The first true "mixed-sandwich" complexes in which a transition metal is bonded to a h^3-poly-1-pyrazolylborate or h^3-poly-1-pyrazolylmethane ligand as well as to a h^4-cyclobutadienyl, (M = Co), h^5-cyclopentadienyl (M = Co, Rh) or h^6-arene, (M = Ru), ligand have been synthesised and characterised.

The chemistry of the poly-1-pyrazolylborate and poly-1-pyrazolylmethane ligands, $\{H_nB\,Pz_{4-n}\}^-$ and $H_nC\,Pz_{4-n}$, (Pz = 1-pyrazolyl) has recently been reviewed[1,2]. Transition metal complexes of these ligands with carbonyl, nitrosyl or arylazo co-ligands show a closely parallel chemistry to the isoelectronic cyclopentadienyl analogues. It is surprising therefore that analogues of the metallocenes containing one cyclopentadienyl (or similar) ligand and one poly-1-pyrazolylborate or poly-1-pyrazolylmethane ligand have stubbornly resisted attempted synthesis[1,2]. This communication reports the first successful isolation of several examples of this new class of organometallic complexes.

$$(C_5R_5)Co(CO)I_2 + Pz_3Y \rightarrow \{(C_5R_5)Co\,Pz_3Y\}^{n+}X^-_n$$

(I)

Ia : $R = H$, $Y = BH^-$, $n = 1$, $X = I$
Ib : $R = H$, $Y = BPz^-$, $n = 1$, $X = I$
Ic : $R = H$, $Y = CH$, $n = 2$, $X = I$
Id : $R = CH_3$, $Y = BH^-$, $n = 1$, $X = I$
Ie : $R = CH_3$, $Y = CH$, $n = 2$, $X = PF_6$

$$\{(C_5Me_5)RhCl_2\}_2 + 2Pz_3Y \rightarrow 2\{(C_5Me_5)RhPz_3Y\}^{n+}X^-_n$$

(II)

IIa: $Y = BH^-$, $n = 1$, $X = PF_6$
IIb: $Y = BPz^-$, $n = 1$, $X = PF_6$
IIc: $Y = CH$, $n = 2$, $X = PF_6$

$$(Ph_4C_4)Co(CO)_2I + Pz_3Y \rightarrow \{(Ph_4C_4)CoPz_3Y\}^{n+}X^-_n$$

(III)

IIIa: $Y = BH^-$, $n = 0$
IIIb: $Y = CH$, $n = 1$, $X = PF_6$

$$\{(C_6H_6)RuCl_2\}_2 + 2Pz_3Y \rightarrow 2\{(C_6H_6)RuPz_3Y\}^{n+}X^-_n$$

(IV)

IVa: $Y = BH^-$, $n = 1$, $X = PF_6$
IVb: $Y = BPz^-$, $n = 1$, $X = PF_6$
IVc: $Y = CH$, $n = 2$, $X = PF_6$

Mixed sandwich complexes were prepared by the series of reactions outlined in the scheme and the products were isolated in near-quantitative yield. Similar reactions were attempted with the tris(3,5-dimethyl-1-pyrazolyl)borate anion but yielded only highly unstable products. It is conceivable that the considerable steric demand of the latter ligand[1] forces coordinatively unsaturated structures on the products.

The new pseudo-metallocenes are purple (I), orange (II), red (III) or yellow (IV) crystalline solids which appear to be indefinitely air stable but slightly less so in solution. Complex (Ic) appears to be the least stable. Even so it may conveniently be recrystallised from boiling water although such treatment is always accompanied by some disproportionation and reduction with the formation of $\{HC\,Pz_3\}_2Co^{2+}$.

All of the complexes (I) to (IV) appear to be diamagnetic as evidenced by their highly-resolved ^1H NMR spectra. The resonance positions in these spectra are extremely sensitive to solvent effects. The spectra of the tetra-1-pyrazolylborate derivatives (Ib), (IIb) and (IVb) show two distinct sets of resonances for the pyrazole protons in the ratio 3/1. The uncomplexed pyrazole ring therefore maintains its identity in solution and these complexes involve a stereochemically rigid h^3-BPz_4^- ligand. Similar structures may be reasonably inferred for the remaining complexes.

Attempts to reduce the cobalticenium analogue (Ia) to a neutral cobaltocene-like complex resulted in cleavage of the (C_5H_5)–Co bond and formation of $\{HB\,Pz_3\}_2Co$. Complex (Ia) reacts with CN^- to give a neutral red crystalline product which has not yet been obtained entirely pure. The ^1H NMR spectrum of this complex suggests that CN^- attacks at one of the pyrazole carbon atoms.

The arene complex (IVa) adds hydride ion to give the cyclohexadienyl complex {HB Pz $_3$} Ru(h^5-C_6H_7) (V). This complex exhibits a temperature-dependent ^{1}H NMR spectrum which is consistent with a rotation of the cyclohexadienyl ligand around the c_3-axis of the {HB Pz $_3$} Ru fragment. At room temperature this rotation is slow on the NMR time-scale but it becomes rapid at ca. 50°C.

Several attempts to synthesise mixed-sandwich analogues of titanocene dichloride, ferrocene or nickelocene via reaction of Tl {HB Pz $_3$} with $(C_5H_5)TiCl_3$, $(C_5H_5)Fe(CO)_2Cl$ and $(C_5H_5)Ni(PPh_3)Cl$ were not successful. Highly unstable products were formed in the Ti reaction and the Fe and Ni compounds gave largely {HB Pz $_3$}$_2$M, (M = Fe, Ni).

REFERENCES

1 S. Trofimenko, *Accounts Chem. Res.*, 4 (1971) 17.
2 S. Trofimenko, *Chem. Rev.*, 72 (1972) 497.