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Preliminary communication

INTERACTIONS IN METAL CLUSTERS

III*. RACEMIZATION BARRIERS AND REVERSIBLE HYDROGEN ADDITION OF A SERIES OF CHIRAL CLUSTERS

AGAPIOS AGAPIOU, RICHARD F. JORDAN, LEONARD A. ZYZYCK, and JACK R. NORTON**

Department of Chemistry, Princeton University, Princeton, New Jersey 08540 (U.S.A.)

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Summary

The barriers to racemization in $C_2D_4Cl_2$ of $[Ir\{Fe(P(p\text{-tolyl})_2)(CO)_2(\eta^5\text{-}C_5H_5)\}_2]^+ BF_4^-$ and $[Ir\{Ru(P(p\text{-tolyl})_2)(CO)_2(\eta^5\text{-}C_5H_5)\}_2]^+ BF_4^-$ are 17.5 and 17.8 kcal/mol respectively. Both clusters add H_2 reversibly at 1 atmosphere and room temperature. The former also forms an adduct with H_2 and CO when exposed to both gases simultaneously.

We have previously reported [1] that the chiral polynuclear cation $[Rh\{FePAr_2(CO)_2(\eta^5\text{-}C_5H_5)\}_2]^+ BF_4^-$ (Ia) has a racemization barrier of 12.6 kcal/mol, determined by variable-temperature $\{^{31}P\}$ ^1H NMR of the *p*-tolyl groups. We considered that, as the racemization process involved distortion of the metal—metal bonds, analogous compounds with second- and third-row transition metals should have higher barriers. We now report the preparation and examination of a number of such chiral cationic clusters I.

The synthesis of Ib (the preparation of which has been mentioned briefly by Haines and coworkers [2]) is easily carried out by the method developed for Ia, with $Ir(CO)_2(p\text{-toluidine})Cl$ [3] substituted for $[Rh(CO)_2Cl]_2$.

$$\mathrm{FpCl + PAr_2H \xrightarrow{C_6H_6} Fp(PAr_2H)^+Cl^-}$$

(IIa) Ar = phenyl

$$\mathrm{IIa + Ir(CO)_2(\mathit{p}\text{-toluidine})Cl \xrightarrow[CH_2Cl_2]{1,8\text{-bis(dimethylamino)naphthalene}} (FpPAr_2)_2Ir(CO)Cl}$$

(IIIa) Ar = phenyl

$(Fp = (\eta^5\text{-}C_5H_5)Fe(CO)_2)$ (72% yield from FpCl)

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*For part II see ref. 1.

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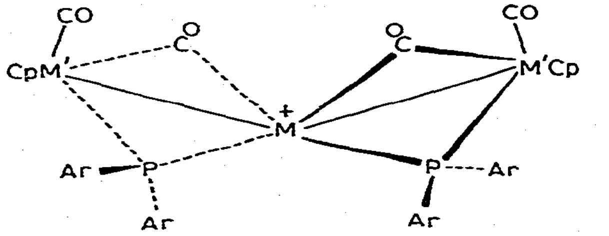


(Ia) M = Rh, M' = Fe, Ar = *p*-tolyl
(Ib) M = Ir, M' = Fe, Ar = phenyl
(Ic) M = Ir, M' = Fe, Ar = *p*-tolyl
(Id) M = Ir, M' = Ru, Ar = phenyl
(Ie) M = Ir, M' = Ru, Ar = *p*-tolyl

$$\text{IIIa} \xrightarrow[\text{THF}]{\text{AgBF}_4} \text{Ib (40\%)}$$

$(\text{Fp} = (\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2)$

The synthesis of the Ar = *p*-tolyl analog (Ic) is easily accomplished by the same general procedure.

The ruthenium analogs Id and Ie require a slight variation. $(\eta^5\text{-C}_5\text{H}_5)\text{Ru(CO)}_2\text{Cl}$ is most easily prepared from $[\text{Ru(CO)}_3\text{Cl}_2]_2$ [4] by a minor modification (aqueous extraction of the product from the filtered reaction mixture) of the method of Stone [5]. Direct reaction with secondary phosphines does not produce the ruthenium analog of the cation IIa above; however, after previous removal of the chloride ligand with silver [6] such a complex can be obtained.

$$(\eta^5\text{-C}_5\text{H}_5)\text{Ru(CO)}_2\text{Cl} \xrightarrow[\text{THF}]{\text{AgBF}_4} \xrightarrow{\text{PAr}_2\text{H}} (\eta^5\text{-C}_5\text{H}_5)\text{Ru(CO)}_2(\text{PAr}_2\text{H})^+\,\text{BF}_4^- \quad (60\%)$$

(IIc) Ar = Ph
(IId) Ar = *p*-tolyl

$$\text{IIc or IId} + \text{Ir(CO)}_2(p\text{-toluidine})\text{Cl} \xrightarrow[\text{acetone}]{\text{tetramethylguanidine}}$$

$$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru(CO)}_2\text{PAr}_2]_2\text{Ir(CO)Cl} \quad (55\%)$$

(IIIc) Ar = phenyl
(IIId) Ar = *p*-tolyl

$$\text{IIIc or IIId} \xrightarrow[\text{THF}]{\text{AgBF}_4} \text{Id or Ie (50\%)}$$

IR spectra of compounds I, II, and III are given in Table 1, and NMR data relevant to the racemization barriers of the compounds I are given in Table 2. Fortunately, in Ic and Ie, unlike Ia [1], the methyl resonances of the inequivalent *p*-tolyl groups are well separated in the low-temperature limit and the NMR analysis is simple. Racemization barriers have indeed increased well above

TABLE 1

CARBONYL REGION IR DATA FOR COMPOUNDS I—VI IN CH_2Cl_2

Compound	ν(CO) (cm^{-1})	Compound	ν(CO) (cm^{-1})
Ib	2010, 1830, 1798	IIIa, IIIb	2025, 1974
Ic	2009, 1827, 1797	IIIc, IIId	2040, 1985
Id	2012, 1840, 1810	IV	2083, 2052, 1990, 1970
Ie	2014, 1837, 1807	V	2041, 2003, 1966
IIa, IIb	2065, 2020	VIa	2068, 2034, 1989
IIc, IId	2072, 2022	VIb	2092, 2052, 2032, 1990

the 12.6 kcal/mol of Ia, showing the expected effect of substitution of Ir for Rh. However, the effect of substitution of Ru for Fe is much smaller.

The $IrRu_2$ cluster Ie dissolves unchanged (by IR) in a much wider variety of solvents than Ia or Ic, permitting the evaluation of solvent effects on the racemization barrier (see Table 2). Although interpretation of solvent effects on rearrangements of a charged molecule is always complicated by inevitable changes in ion-pairing effects, it seems clear that the solvent effect is not particularly large, and that the extent of solvation in the racemization transition state may be less than previously suggested [1].

Our interest in these molecules is of course fundamentally due to their potential as polynuclear homogeneous catalysts [7]. We have therefore examined their reactions with molecular hydrogen and carbon monoxide.

When a solution of the $RhFe_2$ cluster Ia is treated with hydrogen no detectable reaction occurs (although we have not examined the system under pressure). However, a solution of the rust-colored $IrFe_2$ cluster Ib turns burgundy when hydrogen is bubbled through it. Formation of the hydrogen adduct IV is complete within 5 minutes. Furthermore, the reaction is reversible: the characteristic IR bands of Ib appear in a few hours when N_2 is bubbled through a solution of IV, and if the solution is evaporated to dryness and the resulting solid left under vacuum for a day most of the IV is converted back to Ib. (Side reactions, now under investigation, prevent quantitative recovery of Ib). A similar reversible reaction occurs with the $IrRu_2$ cluster Id. The ^1H NMR of IV at 20°C (s, 10H, τ 5.75 ppm; t, J 17 Hz, 2H, τ 32.8 ppm) confirms that it is the adduct of Ib and one equivalent of H_2.

$$\mathrm{Ib} + H_2 \rightleftharpoons \mathrm{IV}$$

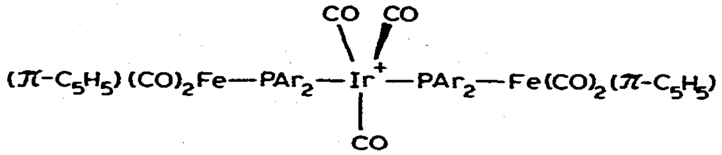
The $IrFe_2$ cluster Ib, like the $RhFe_2$ cluster Ia, forms a CO adduct V. By

TABLE 2

VARIABLE TEMPERATURE ^1H NMR DATA FOR I

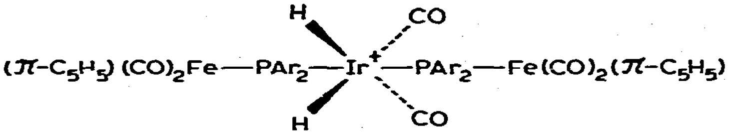
Compound	Solvent	Low temperature limit		$T_{coalescence}$ (°C)	$\Delta G^{\ddagger}_{rac}$ (kcal mol^{-1})
		$\delta(CH_3)$(*p*-tolyl) (ppm)	$\Delta\nu$(tolyl) (Hz)		
Ic	$C_2D_4Cl_2$	2.26, 2.31	4.5	50	17.5
Ie	$C_2D_4Cl_2$	2.32, 2.25	6.2	59	17.8
Ie	$C_2D_4Cl_2$ with 10% EtOH-d_6	2.27, 3.33	5.7	51	17.4
Ie	EtOH-d_6	2.28, 3.33	5.7	61	18.0

analogy to the known [9] IrL$_2$(CO)$_3^+$, and on the basis of its chemistry, it seems likely to have the structure



The formation of this CO adduct V from Ib is for all practical purposes irreversible.

Like Ib, V forms an adduct with hydrogen (VIa). Its ^{1}H NMR (triplet, J 17.5 Hz, τ 18.55 ppm) and infrared spectra (ν(Ir—H) at 2148 cm^{-1}; ν(CO) in Table 1) permit conclusive assignment of its structure. The change in frequency of two carbonyl bands between VIa and the analogous deuterium adduct VIb is definitive evidence that the iridium carbonyl ligands are *trans* to hydride ligands; many complexes of this basic structure are known for simple phosphine ligands [10]. (The light yellow color of V and VI reflects the absence of direct metal—metal interactions, and the chemistry is analogous to that of known mononuclear species [9]).

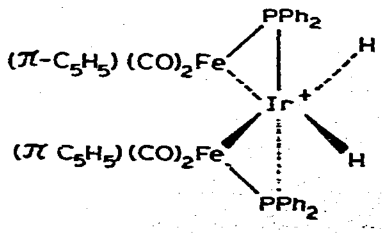


(VIa)

Treatment of VIa with CO reforms the IrFe$_2$ cluster carbonyl adduct V. The cluster Ib thus binds CO more tightly than H$_2$, but the species thermodynamically favored at room temperature and modest pressures is VIa. The complete scheme for adduct formation with Ib is thus:

$$\mathrm{IV} \underset{-\mathrm{H}_2}{\overset{+\mathrm{H}_2}{\rightleftharpoons}} \mathrm{Ib} \xrightarrow{+3\mathrm{CO}} \mathrm{V} \underset{-\mathrm{H}_2,\,+\mathrm{CO}}{\overset{+\mathrm{H}_2,\,-\mathrm{CO}}{\rightleftharpoons}} \mathrm{VIa}$$

Its validity has been confirmed by treating IV, formed from H$_2$ and Ib, with a mixture of H$_2$ and CO overnight: eventually only VIa is present.



(IV)

The structure of IV is unclear. The intense color suggests preservation of the metal—metal bonds; one possibility, consistent with the NMR, is shown.

We have been unable to locate ν(M—H) and cannot rule out bridging hydrides.

To our knowledge, Ib and Id are the first metal clusters reported capable of binding hydrogen reversibly under mild conditions. The complete adduct formation scheme for Ib illustrates the ability of breakable metal—metal bonds to serve as the equivalent of vacant coordination sites in mononuclear complexes.

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