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### Novel behaviour and reactivity in 1,1'-bis(diphenylphosphino)ferrocene and 1,1'-bis(diphenylphosphino)cobaltocene cluster derivatives

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#### Abstract

The clusters  $[Ru_6C(CO)_{16}{Fe}(C_3H_4P(Ph)_2)_2]$  2 and  $[Ru_6C(CO)_{15}{\mu-Fe}(C_5H_4P(Ph)_2)_2]$  3 have been synthesised from the reaction of the parent cluster  $[Ru_6C(CO)_{17}]$  1 with 1,1'-bis(diphenylphosphino)ferrocene (dppf) in THF. The related compound  $[Ru_5C(CO)_{13}\{\mu-Fe}(C_5H_4P(Ph)_2)_2]$  4 is produced from 2 and 3 in more forcing conditions. Both clusters 3 and 4 have been structurally characterised by single crystal X-ray analysis. In 3 the dppf ligand is coordinated in the vicinal form and the cluster core is a highly distorted octahedron. In 4 the vicinal mode is retained but the dppf ligand is coordinated to adjacent basal atoms of a square-base pyramid. The <sup>31</sup>P-NMR spectra of 3 and 4 in CD<sub>2</sub>Cl<sub>2</sub> at various temperatures show a high degree of stereochemically non-rigid behaviour. Magnetic susceptibility measurements across a range of temperatures indicate that 3 is paramagnetic at all temperatures. An electrochemical study of 1, 3, 4 and the related [ $Ru_6C(CO)_{15}\{\mu-G(C)_{15}\{\mu-G(C)_{15}\{\mu-P(Ph)_2)_2\}$ ] 7 has also been synthesised from the direct reaction of the parent cluster [ $Ru_5C(CO)_{15}\{\mu-G(C)_{15}\{\mu-P(Ph)_2)_2\}$ ] 7 has also been synthesis of the dppc analogue of 3 was attempted but was thwarted by unfavourable redox chemistry. EPR spectra have been obtained for both dppc and 7. The oxidation product of 7 has also been produced (7<sup>+</sup>) and displays a high degree of stereochemically non-rigid behaviour in a fashion similar to 3 and 4. The magnetic succeptibility of 7 has also been measured, showing an extraordinarily large magnetic moment at ambient temperature. © 1998 Elsevier Science S.A. All rights reserved.

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#### 1. Introduction

Metallocenes, in particular ferrocene, possess properties which have led to their use as ferromagnets ([1,2]a,b), molecular sensors [3-5] and as electrochemical agents ([6]a). In particular, the relatively high electron-transfer rates of metallocenes ([6]b) make make their incorporation into redox-active systems attractive. Clusters have also been shown to possess unusual magnetic ([7-9]a,b,c) and redox properties [10] which, as far as we are aware, have not been commercially exploited. The idea of combining the properties of these two sets of molecules has significant appeal, and in this paper we report the synthesis and study of the new cluster compounds [Ru<sub>6</sub>C(CO)<sub>16</sub>{Fe(C<sub>3</sub>H<sub>4</sub>P(Ph)<sub>2</sub>)<sub>2</sub>] **2**, [Ru<sub>6</sub>C-(CO)<sub>15</sub>{ $\mu$ -Fe(C<sub>3</sub>H<sub>4</sub>P(Ph)<sub>2</sub>)<sub>2</sub>] **3**, [Ru<sub>5</sub>C(CO)<sub>13</sub>{ $\mu$ -Fe(C<sub>3</sub>H<sub>4</sub>P(Ph)<sub>2</sub>)<sub>2</sub>] **3**, [Ru<sub>5</sub>C(CO)<sub>13</sub>{ $\mu$ -Fe(C<sub>3</sub>H<sub>4</sub>P(Ph)<sub>2</sub>)<sub>2</sub>] **4** and [Ru<sub>5</sub>C(CO)<sub>13</sub>{ $\mu$ -Co(C<sub>3</sub>H<sub>4</sub>P(Ph)<sub>2</sub>)<sub>2</sub>] **7**, along with a wider electrochemical study of related cluster compounds.

There are many reports in the literature of 1,1'-bis(diphenylphosphino)ferrocene (dppf) coordinated to single transition-metals [11]. Some of these heterobimetallic complexes show interesting co-operative effects between the two different metal sites. However,

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few corresponding cluster derivatives of dppf have been reported and these are mainly of low nuclearity [12]. An in-depth review of dppf containing compounds, comparing their structures, synthesis and catalytic properties, can be found in 'Ferrocenes' ([12]c). Reports of paramagnetism in cluster complexes are also relatively few, and the phenomenon is poorly understood ([7– 9]a,b,c). A short communication on this work has recently been published ([9]d).

The didentate ligand 1,1'-bis(diphenylphosphino)cobaltocene (dppc) is similar to the well-known ligand doof but with the added feature of being a paramagnetic 19-e species. Air and water sensitivity are a result of this property, and these features coupled with a complex oxidation behaviour make dppc a little investigated compound [20-22]. There are two methods described in the literature for the synthesis of dppc and for the oxidised 1,1'-bis(diphenylphosphino)cobaltocenium hexafluorophosphate (dppc+) ligand. Rudic et al. [20] published the synthesis for dppc+ in 1978 and compared it to the isoelectronic dppf. They reacted sodium cyclopentadienide with chlorodiphenylphosphine to yield diphenylphosphino-cyclopentadiene from which they abstracted one hydrogen with nbutyl lithium. Cobalt chloride was added and dppc formed, although this was not isolated. Instead, an oxidation using oxygen and acetic acid was performed, yielding 20% dppc+. Several chromium, molybdenum and tungsten carbonyls as well as copper and cobalt halide complexes were reacted with dppf and dppc+ and the products were investigated using IR and UV spectroscopy.

DuBois et al. [21] used thallium ethoxide instead of *n*-butyl lithium to abstract hydrogen from the substituted cyclopentadiene and altered some conditions of the synthesis. They isolated dppc and dppc<sup>+</sup> and used both for further experiments. X-ray structures together with MO calculations and syntheses of Mo carbonyl adducts were reported. The solid-state molecular structure of dppc consists of a Co(II) ion coordinated by two inversion related  $\eta^{5}$ -C<sub>5</sub>H<sub>4</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> ligands. The substituted cyclopentadienyl (Cp) rings deviate slightly from planarity. This group also tried in vain to record an EPR spectrum of dppc.

A recent publication by Wrighton et al. [22] reports the possibility of tuning the redox potential, reactivity, and CO-stretches in the IR spectrum of several rhenium carbonyl complexes where dppc has replaced two carbonyl ligands. The properties of these molecules change noticeably as the oxidation state of the ligand is altered, for instance the rate at which the CO ligands undergo nucleoplilic attack. Kinetic studies and X-ray structure determinations were also reported but no new synthetic route to the title ligand was employed. The almost identical structure of dppc in the different oxidation states when attached to rhenium centre made it possible to attribute all observations to the oxidation state of the dppc ligand.

#### 2. Results and discussion

A summary of the following reactions involved in the production of 2, 3 and 4 is given in Scheme 1.

# 2.1. The preparation of $[Ru_6C(CO)_{16}{Fe(C_5H_4P(Ph)_2)_2}]$ 2

The reaction of dppf with the parent cluster [Ru<sub>6</sub>C(CO)<sub>17</sub>] 1 in THF under reflux for a short reaction time yields  $[Ru_6C(CO)_{16}\{dppf\}]$  2 as the major product along with smaller amounts of [Ru<sub>6</sub>C(CO)<sub>15</sub>{µ- $Fe(C_{3}H_{4}P(Ph)_{2})$ ] 3. After separation by TLC using CH<sub>2</sub>Cl<sub>2</sub>:hexane (1:4) as eluent, dark-green 3 and red 2 were tentatively identified on the basis of their IR spectra. The IR spectrum  $(v_{CO})$  of 2 in dichloromethane is very similar to that of Ru<sub>6</sub>C(CO)<sub>16</sub>PPh<sub>3</sub> ([9]e). Solutions of 2 at room temperature (r.t.) slowly yield 3 and attempts to crystallise 2 from a variety of different solvents at low temperature gave only crystals of 3 after a period of ca. 2 months. Similar problems occured in attempts to obtain the 'H-NMR spectrum of 2 because of the presence in solution of small amounts of paramagnetic 3 (vide infra). However, multiplets were observed in the appropriate regions. Positive ion fast atom bombardment mass spectrometry, an analytical tool normally invaluable to the cluster chemist, gave no molecular ion peak or any recognisable cluster fragments. Peaks at 554, 571 and 587 m/z were observed for 2, 3 and 4 attributable to dppf+ and the phosphine oxides dppfO<sup>+</sup> and dppfO<sub>2</sub><sup>+</sup>, respectively.

#### 2.2. $[Ru_6C(CO)_{15}\{\mu - Fe(C_5H_4P(Ph)_2)_2\}]$ 3

Longer reaction times in THF or cyclohexane gave much improved yield of 3. Separation of the products by TLC, using dichloromethane:hexane as eluent (1:3 v/v), gave 3 as the major product along with some 2 and a trace of 4. The IR spectrum of 3 shows a shift to lower energy for the absorptions in the carbonyl region when compared to those displayed by the parent cluster 1 and the precursor 2. This is indicative of the electronrich nature of 3. The <sup>1</sup>H-NMR spectrum of 3 in CDCl<sub>3</sub> showed exceptionally poor resolution of both the phenyl and Cp resonances at both r.t. and 223 K. This immediately suggested unusual behaviour of the new cluster derivative. A <sup>31</sup>P-NMR spectrum of 3 obtained at 298 K showed a single, slightly broadened signal at ca.  $\delta$  44 ppm. This may be attributed to stereochemically non-rigid behaviour, of both the dppf and cluster core moieties, producing equivalence of the two phosphorus nuclei on the NMR time scale (vide infra). At



O

Ξ

υ

 $\overline{\Omega}$ PPh2

0



c

9

ε



Fig. 1. The solid state molecular structure of 3 as determined by X-ray crystallography. The hydrogen atoms and phenyl groups have been omitted for clarity.

198 K, however, the <sup>31</sup>P-NMR spectrum showed two signals at  $\delta$  41.07 and 52.96 ppm. The high frequency signal was significantly broadened, possibly due to the presence of proximal unpaired electrons. At the coalescence temperature of 218 K and  $\Delta v = 1724$  Hz.  $k_c =$ 3830 s<sup>-1</sup> [26], giving an activation energy or fluxional barrier of  $\Delta G_c^{\neq} = 37.9$  kJ mol<sup>-1</sup> [27]. The two signals observed at low temperature are consistent with the two phosphorus environments observed in the solid state structure of 3.

A single crystal X-ray analysis of 3 was undertaken to establish the molecular structure which is shown in Fig. 1 along with selected structural parameters in Table 2. Of striking significance is the distorted  $Ru_6C$ metal core. Two very long Ru-Ru distances (Ru(1)– Ru(6) 3.171(1), Ru(4)-Ru(6) 3.450(1) Å) are observed and show an 'opening up' of the normally *closo* octahedron to give a hinged square-based pyramid. Ru(6) is hinged at the basal metal atoms Ru(2) and Ru(5) and supported by P(1) of the bridging dppf ligand. All remaining Ru–Ru bonds are within the normal range. The carbido carbon atom is displaced from the centroid of the four metals constituting the base of the squarebased pyramid by 0.217(8) Å towards Ru(6). The distorted cluster is surrounded by 13 terminal carbonyls and two  $\mu$ -COs triangulating the Ru(2)–Ru(3) and Ru(3)–Ru(4) vectors. Single crystal X-ray structural determination has shown that no comparable distortion occurs in either [Ru<sub>6</sub>C(CO)<sub>15</sub>{ $\mu$ -dppm}] 5 [13] or [H<sub>4</sub>Ru<sub>4</sub>C(CO)<sub>10</sub>{ $\mu$ -diphos}] [14].

The dppf is ligated in the vicinal form, bridging the hinged metal Ru(6) and the basal metal Ru(1). Each P atom occupies a slightly distorted tetrahedral environment which, due to the bonding mode and rearrangement of the metal core are nonequivalent. The relative orientations of the P atoms with respect to the ferrocene moiety show a twist of 73.7°. The Cp rings are parallel to within estimated error, eclipsed to within 2.0° and produce an average distance of 1.635(4) Å from their centroids to the iron. The crystal structure

also contains highly disordered dichloromethane solvate molecules.

Magnetic susceptibility measurements show 3 to be paramagnetic at all temperatures (Fig. 2). The corrected data were fitted to both a Curie and a Curie-Weiss expression plus a temperature independent paramagnetic (TIP) term. The quality of the fit was appreciably better when a small Curie-Weiss constant  $\Theta$  of -0.50K was included, and the corresponding values of the Curie constant C and TIP contributions were 0.12 emu K mol<sup>-1</sup> and 0.052*C*, respectively. The value of *C* corresponds to an effective magnetic moment ( $\mu_{eff}$ ) of 0.99(5) BM at high temperatures. It appears therefore that the moment on the ferrocene/cluster unit is 35% of the moment that would arise from a spin triplet state, and that there is a weak antiferromagnetic coupling between the units. The ESR spectrum of a solid sample of 3 appears silent at both 77 and 298 K. This is taken to be consistent with the high rate of relaxation that may be expected for both moieties [17]. The compounds 1, 4, 5 and 6 and dppf are diamagnetic.

A related paramagnetic hexanuclear carbonyl compound has been synthesised by Chini et al. ([7]c). Solutions of the Na<sup>+</sup> or [NMe<sub>3</sub>(CH<sub>2</sub>Ph)]<sup>+</sup> saits of the trigonal prismatic [Co6C(CO)15]2- hexanuclear cluster were treated with CO under ambient conditions to give a mixture of compounds including the dark brown paramagnetic anion [CosC(CO)14]-. A second route to this cluster was devised by which Co<sub>3</sub>(CO)<sub>9</sub>RCl was treated with two molar equivalents of Na[Co(CO)<sub>4</sub>] in diethyl ether. The researchers were able to record an ESR spectrum (THF), however, they only state a gvalue (2.0128) and no cobalt hfs tensor is mentioned. The paramagnetism of the bulk compound was confirmed by Evan's method ([17]b) giving r.t. magnetic moment ( $\mu_{eff}$ ) of 1.37 BM. The molecular structure of this 87-e hexanuclear 'octahedral' cluster is very unusual and bears close resemblance to the structure observed for 3. The metal framework is a distorted



Fig. 2. Variation of molar magnetic susceptibility of 3 with temperature. Superimposed on the data points is a line of best fit utilising the Curie-Weiss expression.

octahedron of idealised molecular symmetry  $C_{2\nu}$ . The 12 Co–Co distances may be divided into three sets: one elongated edge 2.96(1) Å, six carbonyl bridged edges of mean length 2.53 Å and five edges of intermediate lengths (mean 2.75 Å). The authors infer that this structural distortion from that of a regular octahedron is a consequence of the 'extra' unpaired electron.

#### 2.3. $[Ru_5C(CO)_{13}\{\mu - Fe(C_5H_4P(Ph)_2)_2\}]$ 4

The synthesis of 4 from 2 represents a novel example of redox-centre facilitated cluster de-capping. The conversion of 1 to 6 requires high pressures of CO (80 atm) [19]. Heating 2 in octane at reflux gives the dppf ligated nido-cluster compound 4 in high yield. Likewise, 3 can be converted to 4 in comparable yield under similar reaction conditions. Separation of the products was achieved by TLC on silica using dichloromethane: hexane (2:3 v/v) as eluent. Bright pink 4 was extracted with dichloromethane as the major product. A second, more direct route to 4 via the unsubstituted nido-cluster [Ru<sub>5</sub>C(CO)<sub>15</sub>] 6 gave an improved yield and only one product. This short reaction time, as compared to subtitution reactions of the closo-cluster 1, perhaps indicates that the mechanism is an associative one involving bridged-butterfly intermediates which subsequently revert to the square-based pyramid with concomitant expulsion of CO (Scheme 2).

The <sup>1</sup>H-NMR spectrum of 4 in CD<sub>2</sub>Cl<sub>2</sub> was poorly resolved at r.t. On cooling to 218 K line shapes improved greatly, although some broadening is still apparent. These observations are consistent with stereochemical non-rigid behaviour. Similar solution characteristics have been observed previously in monometal compounds containing the dppf ligand [11,12]. These compounds display the geminal coordination mode and hence undergo potentially higher energy processes. Conversely, the vicinal form of coordination displayed in 4 gives greater freedom for non-rigid behaviour (see Salter et al. [12]d). The process is conceivably a combination of two modus operandi: (a) Cp ring twisting, which averages to give the eclipsed formation and (b) inversion at the phosphorus atoms. The <sup>31</sup>P-NMR spectrum of 4 in CD<sub>2</sub>Cl<sub>2</sub> showed a single broadened signal at r.t. but on cooling to 218 K the peak collapsed giving two signals of equal intensity with similar chemical shifts. The stereochemical requirements of the vicinal mode of coordination in 4 demands inequivalence of the phosphorus atoms, as is seen in the solid state structure (vide infra). The low temperature limiting spectrum is therefore consistent with the solid state structure.

The solid state molecular structure of 4 is shown in Fig. 3 and selected structural parameters are found in Table 3. The penta-metallic cluster core is an irregular square-base pyramid partly encapsulating a  $\mu_5$ -C atom.



Fig. 3. The solid state molecular structure of 4 as determined by X-ray crystallography with inserted projections showing the near eclipsed ferrocene and the distorted metal core.



Scheme 2. Possible mechanistic steps involved in the formation of 4 from 6 and dppf.

The eight M-M contacts lie in the range 2.9922(13)-2.794(2) Å, the longest of which [Ru(1)-Ru(4)] is bridged by the phosphines of the dppf ligand. The carbido atom is displaced from the mean plane of the four metals that constitute the base of the pyramid by 0.218(12) Å, away from the apex [Ru(5)]. Along with the dppf ligand, 13 terminal carbonyls make up the ligand cage of the *nido*-cluster.

The dppf moiety is ligated in the vicinal form formally replacing two axial carbonyls of the known  $Ru_5C(CO)_{15}$  cluster. The Ru-P bonds [Ru(1)-P(1),<math>Ru(4)-P(2)] appear to be orientated such that they are ca. collinear with the apical to basal Ru-Ru contacts [Ru(1)-Ru(5), Ru(4)-Ru(5)]. The ferrocenyl group occupies a position proximal to the base of the cluster. The relative orientations of the P atoms with respect to the ferrocene moiety show a twist of 82.4°. The Cp rings are parallel to within estimated error, eclipsed to within 9.8° and produce an average distance of 1.658(6) Å from their centroids to the iron.

#### 2.4. The electronic specta of 1, 3 and dppf

The UV-vis spectra of metallocenes has proven to be a useful tool for probing subtle changes in electronic character of an encapsulated metal atom. The unusual green colour of 3 immediately suggested an electronic character significantly different to red 5. Details of the electronic spectra and their interpretations for TM carbonyl clusters are unfortunately lacking in the literature. In this work the electronic spectra of 1, 3 and dppf were measured in  $CH_2CI_2$  solution at ambient temperature and the data are presented in Table 1, while relevant bond lengths and angles for 1 and 3 are presented in Tables 2 and 3, respectively.

The spectrum for dppf may be interpreted by comparison with that of ferrocene [29]. As shown in Fig. 4, the ground state electronic configuration of dppf may be taken to be  $(e_{2g})^4(a'_{1g})^2$ , the HOMO being predominantly of  $dz^2$  character. The maximum at 439 nm is assignable to the Laporte forbidden transition from the HOMO to LUMO (i.e.  $a'_{1c} \rightarrow e^{*}_{1c}$ ). The low absorption coefficient is consistent with this. The higher energy maximum at 249 nm with a very large absorption coefficient ( $\epsilon = 32020 \text{ M cm}^{-1}$ ) may be assigned to a metal to solvent charge transfer band, and is consistent with the behaviour observed for ferrocene [29].

 $\operatorname{FeCp}_2 + \operatorname{CCl}_4 \rightarrow \operatorname{FeCp}_2^+ + \operatorname{Cl}^- + \operatorname{CCl}_3^{\bullet}$ 

 $dppf + CH_2Cl_2 \rightarrow dppf^+ + Cl^- + CH_2Cl^*$ 

However the removal of an electron from this MO, to give dppf<sup>+</sup> (cf. ferrocenium ion), gives the electronic configuration  $(a'_{1g})^2(e_{2g})^3$  wherein the HOMO is now orbitally degenerate and of mainly dxy,  $dx^2 - y^2$  character (Fig. 5).

The ferrocenium ion (Fc<sup>+</sup>) itself has a remarkable electronic structure. The HOMO has been established as the orbitally degenerate e32g, in contrast to ferrocene in which the HOMO is the filled at the noteworthy inversion of the HOMO and the SHOMO has been established by Raman, UV-vis (at ambient temperature and low temperature), IR and EPR spectroscopic measurements ([29]b). The electronic spectrum of Fc+ gives a strong absorption at 620 nm and may be assigned as the symmetry allowed transition  ${}^{2}E_{2e}(e_{1\mu}^{4}a_{1e}^{2}e_{2e}^{3}) \rightarrow {}^{2}E_{1\mu}(e_{1\mu}^{3}a_{1e}^{2}e_{2e}^{4})$  LMCT. This absorption accounts for the strong blue-green colour of ferrocenium salts. Compound 3 may indeed contain such a ferrocenium like electronic configuration with the transferred electron occupying an anti-bonding skeletal cluster MO, consistent with the structural and magnetic evidence shown above. Green 3, like ferrocenium, shows a strong absorption in this region (600 nm,  $\epsilon = 5074$  M cm<sup>-1</sup>) and may be assigned either to a similar symmetry allowed " ${}^{2}E_{2g} \rightarrow {}^{2}E_{1u}$ " within the dppf domain or a 'cluster to ferrocenium' transition "M- $M^* \rightarrow {}^{1}E_{1u}$ ". However, this feature is very broad at ambient temperature and may mask a more complex set of electronic transitions available to 3. Hence this evidence suggests that the electronic structure of the metallocene unit is significantly altered cf. dppf and is

Table 1 Electronic absorption spectral data for 20, dppf, 22

Compound	λ (nm)	ε (M cm <sup>-1</sup> )	Assignment
1	320(sh)		_
	417(m)	18880	$M-M \rightarrow M$
			·M*
dppf	249(m)	32020	MSCT
	439(m)	354	d-d
	886(m)	224	
3	333(sh), 414(m)	16220, 11640	$M - M \rightarrow M$
			M*
	600(m)	5074	$M - M^* \rightarrow {}^1E$

consistent with the description of **3** as a stable structurally-mediated CT induced triplet state Zwitterion. The orbitally degenerate triplet ground state in **3**, in both the cluster and dppf domains, may explain the silence of the EPR even at 77 K.

#### 2.5. Electrochemical investigations

Shifts in the redox potential of the dppf ligand and Ru clusters are of great interest and demonstrate in a complementary fashion electronic and/or electrostatic communication between redox active sites [15]. Electrochemical data for compounds 1, 3, 4, 5 and 6 given in Table 4.

The parent cluster I exhibits no oxidative process but a 2-e reduction at -0.46 V to yield  $[Ru_6C(CO)_{16}]^{2-1}$ which oxidises at +0.45 V [16]. We have re-examined this reduction at low temperature (223 K) and have found that the 2-e reduction is split into two 1-e steps at -0.36 and -0.69 V. Free dppf undergoes a quasi-reversible oxidation at +0.75 V, assigned primarily to the Fe<sup>II</sup>/Fe<sup>III</sup> couple. Cyclic voltammetry of 3 in 0.5 M [n-Bu<sub>4</sub>N][BF<sub>4</sub>] in CH<sub>2</sub>Cl<sub>2</sub> solution at r.t. reveals an irreversible 2-e reduction at -0.65 V versus Ag|AgCl with associated daughter peaks at +0.07 and +0.25V. This reductive proess remains a single 2-e step at 223 K. An irreversible oxidation is observed at ca. + 1.15 V. Bulk electrolysis at -0.80 V confirms the reductive process as a 2-e step (n = 1.95). By inspection the oxidative process involves 1-e. Coulometric studies of the oxidative process were hampered because of adsorption at the positive potential. Characterisation the daughter products of the reductive process is under way. An examination of the cyclic voltammetry of 5 shows no oxidative process but an irreversible 2-e reductive process at -0.71 V with an attendant daughter peak at +0.23 V. The cathodic shift of the reduction potential displayed in 5 compared to that of the parent cluster 1 can be explained in terms of the increased cluster electron density provided by the didentate phosphine ligand (dppm). The existence of only one daughter peak in the return wave of the cyclic voltammogram of 5 suggests a different redox mechanism to that of 3. This is likely to be due to the different cluster geometries in 3 and 5. We therefore assign the 2-e reduction of 3 as primarily cluster based and the oxidation as primarily dppf based.

The cyclic voltammetry of 4 in 0.5 M [*n*-Bu<sub>4</sub>N][BF<sub>4</sub>] in CH<sub>2</sub>Cl<sub>2</sub> solution at r.t. shows the same dppf based oxidation and a 2-e cluster reduction at +1.06 and -1.05 V with attendant daughter peaks at -0.15 and -0.21 V, respectively. The related cluster [Ru<sub>5</sub>C(CO)<sub>15</sub>] 6 exhibits an irreversible 2-e oxidative process at +0.49V. The expected 2-e reduction at -0.63 V to yield [Ru<sub>5</sub>C(CO)<sub>14</sub>]<sup>2-</sup>, which oxidises at ca. -0.20 V on the return wave, can only be observed at low temperature

Table 2 Selected bond lengths (Å) and angles (°) for 3 with estimated S.D. in perentheses

Bond length (Å)					
Ru(1) - C(12)	1,855(8)	$R_{0}(1) - C(11)$	1.896(8)	Ru(1)-C	1.996(7)
$Ru(1) \sim P(2)$	2.391(2)	Ru(1) - Ru(4)	2.8703(10)	Ru(1) - Ru(3)	2.9122(10)
$Ru(1) \sim Ru(2)$	2.9676(10)	$R_{11}(2) = C(22)$	1.840(7)	$R_{11}(2) - C(21)$	1.872(8)
$Ru(2) \sim C(23)$	2.005(7)	$R_{\mu}(2) - C$	2.135(7)	Ru(2) - Ru(3)	2.7674(11)
$Ru(2) \sim Ru(6)$	2.8145(10)	$R_{II}(2) - R_{II}(5)$	2.9712(10)	Ru(3) - C(31)	1.851(8)
$R_{11}(3) \sim C(32)$	1.891(8)	$R_{11}(3) - C(41)$	2.170(8)	Ru(3)-C	2.204(7)
$R_{11}(3) \sim C(23)$	2.230(7)	$R_{11}(3) - R_{12}(4)$	2.8542(10)	$R_{11}(3) - R_{11}(5)$	2.9142(12)
$R_{11}(4) \sim C(43)$	1.875(8)	Ru(4) - C(42)	1.903(8)	$R_{4}(4) - C(41)$	2.015(8)
Ru(4)~C	2.044(7)	Ru(4) - Ru(5)	2.8267(10)	$R_{11}(5) - C(53)$	1.905(8)
Ru(5)~C(51)	1.918(8)	$R_{1}(5) - C(52)$	1,929(8)	Ru(5)-C	2.089(7)
Ru(5)~Ru(6)	2.8610(11)	$R_{II}(6) - C(61)$	1.818(7)	Ru(6) - C(62)	1.860(7)
Ru(6)~C	2.105(7)	$R_{u}(6) - P(1)$	2.389(2)	P(1)-C(1F)	1.811(7)
P(1) - C(1P)	1.831(7)	P(1) - C(7P)	1,841(8)	P(2)-C(13P)	1.806(7)
P(2) - C(6F)	1.819(7)	P(2) - C(19P)	1.854(8)	C(1F)~C(5F)	1.409(10)
$C(1F) \sim C(2F)$	1.413(10)	C(2F) - C(3F)	1.385(11)	C(3F)~C(4F)	1.397(11)
C(4F)~C(5F)	1.405(11)	C(6F)-C(7F)	1.411(10)	C(6F)C(10F)	1.436(10)
C(7F) - C(8F)	1.367(11)	C(8F)-C(9F)	1.416(11)	C(9F)~C(10F)	1.403(11)
$C(1P) \sim C(6P)$	1.386(11)	C(1P) - C(2P)	1,390(10)	C(2P)~C(3P)	1.381(11)
$C(3P) \sim C(4P)$	1.409(12)	C(4P) - C(5P)	1.443(11)	C(5P)~C(6P)	1.384(11)
C(7P) - C(12P)	1.362(11)	C(7P) - C(8P)	1.382(11)	C(8P)-C(9P)	1.396(11)
C(9P)~C(10P)	1.382(12)	C(10P) - C(11P)	1.373(12)	C(11P) - C(12P)	1.405(12)
C(13P) - C(14P)	1.401(11)	C(13P)-C(18P)	1.432(10)	C(14P)-C(15P)	1.347(11)
C(15P) - C(16P)	1.385(12)	C(16P)-C(17P)	1.386(12)	C(17P)-C(18P)	1.370(11)
C(19P) - C(24P)	1.352(11)	C(19P)-C(20P)	1.379(11)	C(20P) - C(21P)	1.428(11)
C(21P)~C(22P)	1.335(12)	C(22P)-C(23P)	1.350(12)	C(23P)-C(24P)	1,398(11)
Dend unels (0)					
Bond angle (")	111 67(6)	B(2) Bu(1) Du(2)	164 03(5)		
$\Gamma(2) = \Gamma(0(1) = \Gamma(0(4))$ $\Gamma(0(4) = \Gamma(0(1)) = \Gamma(0(4))$	50 15(2)	P(2) = Ru(1) = Ru(3) P(2) = Ru(1) = Ru(2)	120 65(5)		
$Ru(4) \sim Ru(1) - Ru(3)$	59.15(5) 00.17(3)	$P(2) \sim Ku(1) - Ku(2)$ $P_{11}(2) = P_{12}(2)$	139.03(3)		
Ru(4) - Ru(1) - Ru(2) Pu(2) = Pu(3) = Pu(6)	90.17(3)	$R_{u}(3) = R_{u}(1) = R_{u}(2)$	60.02(2)		
$Ru(3) \sim Ru(2) - Ru(0)$	99.07(3)	Ru(3) = Ru(2) = Ru(1) Ru(2) = Ru(2) = Ru(5)	60.92(2)		
Ru(0) - Ru(2) - Ru(1) Ru(6) - Ru(2) - Ru(1)	50 20(2)	$P_{11}(1) = P_{11}(2) - P_{11}(5)$	86 60(3)		
Ru(0) - Ru(2) - Ru(3) Ru(2) - Ru(3)	39.20(3) 04.60(2)	$R_{u}(1) = R_{u}(2) - R_{u}(3)$	60.09(3)		
$Ru(2) \sim Ru(3) - Ru(4)$ Ru(4) = Ru(3) = Ru(1)	50 60(2)	$R_{u}(2) = R_{u}(3) = R_{u}(1)$ $R_{u}(2) = R_{u}(3) = R_{u}(5)$	63 00(2)		
$Ru(4) \sim Ru(3) - Ru(1)$ Ru(4) = Ru(2) = Ru(5)	59 69(2)	Ru(2) = Ru(3) - Ru(3) Ru(1) = Ru(2) = Ru(5)	03.00(2)		
$Ru(4) \sim Ru(3) - Ru(3)$	20.00(2)	$Ru(1) = Ru(3) \sim Ru(3)$ Ru(5) = Ru(4) = Ru(1)	01 27(2)		
$Ru(3) \sim Ru(4) - Ru(3)$ Ru(2) = Ru(4) = Ru(1)	61.72(3)	$Ru(3) = Ru(4) \sim Ru(1)$ Ru(4) = Ru(5) = Ru(6)	74 71(2)		
$Ru(3) \sim Ru(4) - Ru(1)$ Ru(4) = Ru(5) = Ru(3)	59.60(2)	Ru(4) = Ru(5) - Ru(0) Ru(6) = Ru(5) - Ru(3)	94 67(3)		
Ru(4) - Ru(5) - Ru(5)	00.05(3)	$R_{u}(6) = R_{u}(5) - R_{u}(2)$	57 67(2)		
Ru(3) = Ru(5) = Ru(2)	56 08(3)	P(1) = P u(6) = P u(7)	170 30(5)		
P(1) = Ru(6) = Ru(5)	125 32(5)	$R_{1}(2) = R_{1}(6) = R_{2}(5)$	63 13(3)		
$R_{H}(1) = C = R_{H}(4)$	90 5(3)	$Ru(1) = C \sim Ru(5)$	172.7(4)		
Ru(4) = C = Ru(5)	86 3(3)	Ru(1) = C - Ru(6)	101 3(3)		
Ru(4) = C = Ru(6)	112 5(3)	Ru(5) = C = Ru(6)	86.0(3)		
Ru(1) = C = Ru(2)	91.8(3)	Ru(4) = C - Ru(2)	163 3(4)		
Ru(5) = C = Ru(2)	89.4(3)	Ru(6) = C - Ru(2)	83.2(3)		
Ru(1) = C = Ru(3)	87 7(3)	Ru(4) = C = Ru(3)	84.3(3)		
Ru(5) - C - Ru(3)	85.5(3)	$R_{U}(6) = C \sim R_{U}(3)$	160.5(4)		
Ru(2) = C = Ru(3)	79.2(2)	C(1F) = P(1) = C(1P)	101.1(3)		
C(1F) - P(1) - C(7P)	102.4(3)	C(1P) - P(1) - C(7P)	104.1(3)		
$C(1F) \sim P(1) - Ru(6)$	117.4(2)	C(1P) - P(1) - Ru(6)	109.4(2)		
C(7P) - P(1) - Ru(6)	120.1(3)	C(13P) - P(2) - C(6F)	102.2(3)		
C(13P) - P(2) - C(19P)	99.0(3)	C(6F) - P(2) - C(19P)	105.4(3)		
C(13P) - P(2) - Ru(1)	109.9(2)	C(6F) - P(2) - Ru(1)	119.2(2)		
C(19)-P(2)-Ru(1)	118.1(3)	Ru(2)-C(23)-Ru(3)	81.4(3)		
Ru(4) - C(41) - Ru(3)	85.9(3)				

(223 K). At ambient temperature the 2-e reduction is appears to be split into two 1-e steps at ca. -0.58 and -1.04 V, although the peak shapes are poor. These

investigations show that the cluster and dppf moieties, in 3 and 4, are more difficult to reduce and oxidise, respectively, than either the parent cluster or free dppf.

Bond length (Å)					
Ru(1)-C(12)	1.89(2)	Ru(1)-C(11)	1.897(13)	Ru(1)-P(1)	2.374(3)
Ru(1)-Ru(5)	2.8119(12)	Ru(1)-Ru(3)	2,8841(14)	Ru(1)-Ru(4)	2.9922(13)
Ru(2)-C(21)	1,887(12)	Ru(2)-C(22)	1,89(2)	Ru(2)C(23)	1.947(14)
Ru(2)-Ru(3)	2.7939(13)	Ru(2)-Ru(5)	2.826(2)	Ru(2)-Ru(4)	2.8488(14)
Ru(3)-C(32)	1.88(2)	Ru(3)-C(33)	1.916(12)	Ru(3)C(31)	1.930(12)
Ru(3)-Ru(5)	2.794(2)	Ru(4)-C(41)	1.87(2)	Ru(4)-C(42)	1.884(12)
Ru(4)-P(2)	2.368(3)	Ru(4)-Ru(5)	2.7995(13)	Ru(5)-C(51)	1.902(13)
Ru(5)-C(52)	1.920(11)	Ru(5)-C(53)	1.92(2)	P(1)-C(6F)	1,811(13)
P(1) - C(13P)	1.836(10)	P(1)-C(19P)	1.846(13)	P(2)-C(7P)	1.814(14)
P(2) - C(1F)	1.827(11)	P(2) - C(1P)	1.826(13)	C(1F)-C(5F)	1.39(2)
C(1F)-C(2F)	1.42(2)	C(2F)-C(3F)	1.43(2)	C(3F)-C(4F)	1,39(2)
C(4F)C(5F)	1.42(2)	C(6F)-C(7F)	1.43(2)	C(6F)-C(10F)	1.44(2)
C(7F)-C(8F)	1.41(2)	C(8F)-C(9F)	1,40(2)	C(9F)-C(10F)	1.45(2)
C(1P)-C(2P)	1.38(2)	C(1P)-C(6P)	1.40(2)	C(2P)-C(3P)	1,39(2)
C(3P)C(4P)	1.41(2)	C(4P)C(5P)	1.40(2)	C(5P)-C(6P)	1.37(2)
C(7P) - C(12P)	1.40(2)	C(7P)-C(8P)	1.41(2)	C(8P)-C(9P)	1.38(2)
C(9P) - C(10P)	1.37(2)	C(10P)-C(11P)	1.41(2)	C(11P)-C(12P)	1,39(2)
C(13P)-C(18P)	1.39(2)	C(13P)-C(14P)	1.39(2)	C(14P)-C(15P)	1,39(2)
C(15P)-C(16P)	1.33(2)	C(16P)-C(17P)	1.40(2)	C(17P)-C(18P)	1.36(2)
C(19P)-C(20P)	1.37(2)	C(19P)-C(24P)	1.39(2)	C(20P)-C(21P)	1.39(2)
C(21P)C(22P)	1.37(2)	C(22P)-C(23P)	1.38(2)	C(23P)-C(24P)	1,39(2)
Bond angle (°)					
P(1) - Ru(1) - Ru(5)	157.36(9)	Ru(5)-Ru(1)-Ru(4)	57.57(3)		
Ru(3)-Ru(1)-Ru(4)	87.90(4)	Ru(3)-Ru(2)-Ru(5)	59.62(4)		
Ru(3)-Ru(2)-Ru(4)	92.58(4)	Ru(5)-Ru(2)-Ru(4)	59.12(3)		
Ru(2)-Ru(3)-Ru(5)	60.76(4)	Ru(2)-Ru(3)-Ru(1)	91.36(4)		
Ru(5)-Ru(3)~Ru(1)	59.34(4)	P(2)-Ru(4)-Ru(5)	167.14(10)		
Ru(5)-Ru(4)-Ru(2)	60.03(3)	Ru(5)-Ru(4)-Ru(1)	57.98(3)		
Ru(2)-Ru(4)-Ru(1)	88.11(4)	Ru(3)-Ru(5)-Ru(4)	93.65(4)		
Ru(3)-Ru(5)-Ru(1)	61.93(3)	Ru(4)-Ru(5)-Ru(1)	64.45(3)		
Ru(3)-Ru(5)-Ru(2)	59.62(4)	Ru(4)-Ru(5)-Ru(2)	60.85(3)		
Ru(1)-Ru(5)-Ru(2)	92.22(4)	C(6F)-P(1)-C(13P)	101.5(5)		
C(6F)-P(1)-C(19P)	101.8(6)	C(13P)-P(1)-C(19P)	101.2(5)		
C(6F) - P(1) - Ru(1)	116.7(4)	C(13P)-P(1)-Ru(1)	120,7(5)		
C(19P)-P(1)-Ru(1)	112.2(4)	C(7P) - P(2) - C(1F)	101.6(5)		
C(7P)-P(2)-C(1P)	101.9(6)	C(1F)-P(2)-C(1P)	102.8(5)		
C(7P) - P(2) - Ru(4)	121.8(4)	C(1F)-P(2)-Ru(4)	116.0(4)		
C(1P)-P(2)~Ru(4)	110.3(4)				

Table 3 Selected bond lengths (Å) and angles (°) for 4 with estimated S.D. in perentheses

The mechanisms of the irreversible reductions of the parent clusters 1 and 6 are of great interest. The temperature dependency of these electrochemical transformations suggests that a significant degree of cluster core rearrangement occurs along with the electron transfer process. Possible mechanisms for the electrochemical reduction of both 1 and 6 are given in Figs. 6 and 7, respectively. The LUMO of both clusters is a M-M antibonding cage orbital, thus electron transfer into this orbital invokes a lengthening of the M-M vectors. This distortion may then become localised in the breaking of one or two metal contacts, depending on the steric constraints of the cluster species. The low temperature reduction of 1 involves two 1-e steps, the first of which, at -0.36V, is reversible. This cluster species may be taken to be the ruthenium analogue of the fully characterised isoelectronic cobalt cluster  $[Co_6C(CO)_{14}]^-$  ([7]c). The addition of a second electron is expected to induce greater core distortion to give the hinged square-base pyramid which has the 'correct' structure for the 88 valence electron count. This highly unstable intermediate probably spontaneously ejects CO and reforms the regular octahedron with a standard electron count of 86-e.

The square-base pyramidal geometry of **6** is, by comparison, a much less rigid structure, and this is reflected in its electrochemistry, by way of broad line shapes at ambient temperature. The electrochemical characteristics of cluster compounds are dominated by the geometry of the metal skeleton, reversible electron transfers therefore involve electrons in MOs that are not directly involved in cluster bonding, or if so induce negligible structural change. It is difficult to explain, however, why the observed temperature dependent electrochemical behaviour is the reverse of 1. The addition of 2 e from a suitable donor to 6 has been shown give

122



Fig. 4. A qualitative MO diagram for dppf based on that generally accepted for ferrocene ([29]a).

a carbon centred 76-e bridged-butterfly species, this transformation being accompanied by the breaking of a single M-M contact. By analogy, it is reasonable to assume that the low-temperature reduction follows a similar pathway forming the 76-e bridged-butterfly dianion which spontaneously ejects CO to referm to give the 74-e square-based pyramid dianion.

These results suggest that there is significant interaction between the ferrocene and the cluster cage frontier orbitals in 3 and 4. The magnetic properties and the larger anodic electrochemical shift of the ferrocenyl centre in 3 show an appreciably stronger interaction than that in 4. We propose the HOMO in 3 to be primarily ferrocene based but with significant cage character which results in its increased reluctance to undergo oxidation. Concomitantly the LUMO is primarily cage based but with a significant ferrocene admixture. Increased electron density at the cluster leads to the structural deformation observed in the solid state structure of 3 (Fig. 8). This is perhaps a consequence of the increased electron deficiency of higher nuclearity clusters.

#### 2.6. 1,1'-Bis(diphenylphosphino)cobaltocene (dppc)

To date it appears that, after an extensive literature search, no metal cluster with dppc attached to it has been synthesised. Therefore we set out to synthesise ruthenium and other metal clusters containing dppc as a ligand. An analogous compound with dppf on a hexanuclear ruthenium cluster,  $[Ru_c C(CO)_{15}{\mu-Fe}(C_5H_4P(Ph)_2)_2]$  3, has just been described [24], but the paramagnetic properties and the EPR-active nucleus <sup>59</sup>Co made the replacement of iron by cobalt an interesting proposition.



Fig. 5. A qualitative MO diagram for dppf+ ([29]a-c).

# 2.7. Synthesis of 1,1'-bis(diphenylphosphino)cobaltocene (dppc)

The synthesis was similar to the one given in Rudie et al. [20] until before the oxidation step and also uses some of the methods proposed by DuBois et al. [21].

able 4										
Electrochemical	parameters	oſ	3	and	4	and	some	related	com	olexes

Compound	$E_{1,2}$ Fc (0/1)	$i_{\rm pu}/i_{\rm pc}$	<i>E</i> Ru <sub>6</sub> C (0/~ 11)	i <sub>pu</sub> /i <sub>pe</sub>
Fe(C,H,PPh,),	0.75	0.4	····	
1	_		0,46	0.0
3	1.15	0,0	-0.65	0.1
4	1.06	0,0	- 1.05	0.1
5			0.71	0.0
6			-0.63"	0.0

" At 223 K.

However, some improvements have been made and the whole procedure is given in Section 4.

### 2.8. Reactions with the hexaruthenium carbido cluster $[Ru_6C(CO)_{17}]$

A sample of  $[Ru_6C(CO)_{17}]$  1 was stirred with dppc in THF at ambient temperature and the reaction was monitored by IR spectroscopy. Since the characteristic absorption in the carbonyl region ( $v_{CO} = 1977 \text{ cm}^{-1}$ ) of the cluster anion  $[Ru_6C(CO)_{16}]^{2-}$  was observed together with effervesence as the reaction progressed, the following reaction is believed to have taken place:

 $Ru_6C(CO)_{17}$ 

+  $2Co^{II}[C_5H_4P(C_6H_5)_2]_2 \xrightarrow{-CO} [Ru_6C(CO)_{16}]^2 -$ 

 $+ 2Co^{HI}[C_5H_4P(C_6H_5)_2]_2^+$ 



Fig. 6. Possible mechanisms for the electrochemical transformations available to 1.

The hexaruthenium carbide dianion  $[Ru_6C(CO)_{16}]^2$ was then oxidised in situ by addition of ferrocenium tetrafluoroborate in order to provide a neutral cluster that the nascent dppc<sup>+</sup> could attack (cf. the synthesis of 3).

$$[Ru_6C(CO)_{16}]^{2^-} + Co^{III}[C_5H_4P(C_6H_5)_2]_2^+$$
  
+ 2FeCp<sub>2</sub><sup>+</sup> BF<sup>--</sup>  
→ Ru\_6C(CO)\_{15}{Co^{III}[C\_5H\_4P(C\_6H\_5)\_2]\_2}^+ + 2BF\_4^-  
+ 2FeCp<sub>2</sub> + CO

The products were separated by means of column and thin layer chromatography. For each band, an IR spectrum was recorded and the data from these are collected in Table 5 for comparison.

The second product to be isolated (B2) was initially characterised on the basis of it's IR and positive fast atom bombardment (+FAB) MS. The IR spectrum in the  $v_{CO}$  region closely resembles those for 3 and 4, but is shifted slightly toward higher wave number. Due to the poor solubility of this compound in the +FAB matrix (3-NOBA), some acetonitrile had to be added. A total of 107 scans were necessary to obtain a still noisy



Fig. 7. Possible mechanisms for the reductive electrochemical transformations available to 6.



Fig. 8. A representation of two intramolecular redox states of 3 and their facile interconversion.

spectrum. However, a molecular ion peak could be assigned at m/z = 1437 (64%) which corresponds to  $Ru_sC(CO)_{13}(dppc)^+ 7^+ (M = 1438 g mol^{-1})$  (Fig. 9). This evidence together with the IR spectrum suggests that the  $Ru_sC(CO)_{17}$  cluster has de-capped similarly to the thermally induced conversion of 3 to 4 (vide supra). An improved synthesis of 7 is given later. The first and second products (B1, B3) showed no identifiable peaks in their + FAB MS and no further attempt was made to characterise them.

#### 2.9. <sup>31</sup>P-VTNMR spectra of 7<sup>+</sup>

The <sup>31</sup>P-NMR spectrum of 7<sup>+</sup> in CDCl<sub>3</sub> at ambient temperature gave a single line at ca.  $\delta$  25 ppm. Since it is unlikely that the P atoms could occupy equivalent positions (cf. 4), <sup>31</sup>P-NMR spectra of 7<sup>+</sup> in CD<sub>2</sub>Cl<sub>2</sub> were recorded over a range of temperatures to show any fluxionality in the system. For very slow exchange, both P atoms may be expected to have two distinct resonances since they are not in identical environments. The <sup>31</sup>P-VTNMR of 7<sup>+</sup> gave a series of spectra that could be interpreted as explained above. At the coalescence temperature of 243 K and  $\Delta r = 815$  Hz,  $k_c = 1810$ s<sup>-1</sup> [26], giving an activation energy or fluxional barrier of  $\Delta G_c^{\neq} = 44.0$  kJ mol<sup>-1</sup> [27]. The vicinal form of coordination displayed in 7+ gives greater freedom for non-rigid behaviour as compared to the geminal mode [23]. The process is by analogy with the isoelectronic 4 a combination of three modus operandi: (a) Cp ring twisting, which averages to give the eclipsed formation;

Species	*1/cm <sup>-1</sup>	v <sub>2</sub> /cm <sup>-1</sup>	v <sub>3</sub> /cm <sup>-1</sup>	Y₄/cm <sup>−1</sup>	v <sub>5</sub> /cm <sup>-1</sup>	ν <sub>6</sub> /cm <sup>-1</sup>	ν <sub>7</sub> /cm <sup>−1</sup>
Ru <sub>6</sub> C(CO) <sub>17</sub> 20	2101 (w)	2067 (s)	2047 (vs)	2002 (w)	1834 (w)	_	
[Ru <sub>6</sub> C(CO) <sub>16</sub> ] <sup>2</sup> -	1977 (s)	_					
Mixture before oxidation	2068 (m)	2046 (s)	2022 (m)	2002 (m)	1977 (vs)	1916 (sh)	1775 (w)
(B1) acctone-soluble	2065 (m)	2032 (s)	2008 (vs)	1999 (sh)	1985 (sh)	1952 (w)	1927 (vw)
(B2) acctone-soluble 7+	2079 (s)	2046 (s)	2033 (vs)	2008 (s)	2001 (sh)	1976 (w, sh)	
(B3) acetone-soluble	2039 (sh)	2013 (s)	2006 (sh)	1995 (sh)	1978 (sh)		_

Table 5	
IR spectra of Ru <sub>6</sub> C(CO) <sub>17</sub> derivatives fro	om the reaction with dppc

(b) inversion at the phosphorus atoms; and (c) libration between axial and equatorial sites at the basal ruthenium atoms, involving rotation of the metal's ligand sphere. Because the stereochemically non-rigid behaviour in this molecule is very similar to that observed in 4, it is believed that the ligand dpcc is bound to the cluster in an identical fashion viz. the *vicinal* form to two basal ruthenium atoms in the axial positions which is in accordance with the near superimposability of their IR spectra.

The electrochemical potentials of the following reactions, measured versus Ag|AgCl are:

 $Co^{II}[C_5H_4P(C_6H_5)_2]_2 \rightarrow Co^{III}[C_5H_4P(C_6H_5)_2]_2^+$ 

 $E = -0.56 \text{ V} (\text{in CH}_3 \text{CN}) [22]$ 

 $Ru_6C(CO)17 \xrightarrow{-CO} [Ru_6C(CO)_{16}]^2$ 

 $E = -0.46 \text{ V} (\text{in CH}_2\text{Cl}_2)$ 

 $Ru_5C(CO)_{15} \xrightarrow{-CO} [Ru_5C(CO)^{14}]^2 -$ 

E = -0.63 V (in CH<sub>2</sub>Cl<sub>2</sub>, at  $-50^{\circ}$ C) [11]

One electron reductions are not stable for either of the ruthenium clusters at ambient temperature. Comparing the first and second potential given above, it is clear why the hexaruthenium carbido cluster was reduced by dppc. In order to avoid such a reaction, the pentaruthenium carbido cluster was chosen as the next reaction partner.

#### 2.10. Reaction of dppc with the cluster $Ru_5C(CO)_{15}[Ru_5C(CO)_{13}\{\mu-Co(C_5H_4P(Ph)_2)_2\}]$ 7

This reaction took place at ambient temperature simply by stirring the reactants in THF over several days. In Table 6, the IR absorption frequencies show that the parent cluster  $Ru_5C(CO)_{15}$  is rapidly consumed and a product is formed. After 48 h, the reaction was complete and the IR spectrum was very similar to that of  $[Ru_5C(CO)_{13}(dppf)]$  4 in the  $v_{CO}$  region (vide supra). IR spectroscopy indicated complete consumption of starting material and that no discernible further reaction was occuring; apparently only one product was formed. In analogy to the dppf experiment, the following reaction is believed to have taken place:

#### Ru<sub>5</sub>C(CO)<sub>15</sub> (6)

 $+ Co[C_5H_4P(C_6H_5)_2]_2$  (dppc)

### $\xrightarrow{\sim}{}^{2CO}[Ru_5C(CO)_{13}\{\mu\text{-}Co(C_5H_4P(Ph)_2)_2\}] (7)$

The compounds 4 and 7 are believed to be isostructural. The most important distinction between the IR spectra of 4 and 7 is the absorption band around 2000 cm<sup>-1</sup>; 7 gives a strong and broad band, whereas 4 only gives a medium intensity band. This is thought to be attributable to a much larger donor effect of dppc compared to dppf. Scheme 3 gives the proposed reaction mechanism for the formation of 7 in which Zwitterionic radicals may exist in equilibrium with the normal radical species. This could mean that two distinct forms exist, for each intermediate, which are separated by a potential energy barrier. Favourable energetic wells for the Zwitterions could be the reason why this reaction took 48 h for completion whereas 4 was formed in a very nuch shorter reaction time.

## 2.11. The EPR spectra of dppc and $[Ru_5C(CO)_{13}\{\mu-Co(C_5H_4P(Ph)_2)_2\}]$ 7

Electron paramagnetic resonance is a useful tool in measuring the interaction of an unpaired electron with EPR-active nuclei. <sup>59</sup>Co, with 100% natural abundance, is a nucleus with spin I = 7/2 and thus gives eight lines in an EPR spectrum. Several useful applications of EPR spectroscopy on paramagnetic, organometallic cobalt compounds have been reported [25,29].

Both a powder of pure dppc and a frozen glass solution in THF were used to record spectra at 77 K which are presented in Figs. 10 and 11, respectively. Table 7 contains the collection parameters and calculated hyperfine coupling constants for both dppc and 7 (Fig. 12 shows an EPR spectrum of 7). The powder spectrum of dppc at 77 K resembles a d<sup>9</sup> metal centre with axial symmetry, although the g-values make assignment and hence determination of the ground state configuration ambiguous. We would expect, however, that the unpaired electron occupies the degenerate  $e_{fg}^*$  orbital of predominantly covalent character (dxz, dyz = 58%, Cp = 42%) by analogy with the ground state configuration of CoCp<sub>2</sub> [33]. A molecular orbital



Scheme 3. A possible mechanism for the reaction of the pentaruthenium carbido cluster Ru<sub>5</sub>C(CO)<sub>15</sub> with 1,1'-bis(diphenylphosphino)cobaltocene (dppc).



Fig. 9. <sup>31</sup>P-NMR spectrum of 7<sup>+</sup> in CD<sub>2</sub>Cl<sub>2</sub> at various temperatures, 145 MHz.

diagram for dppc is illustrated in Fig. 13. The frozen solution EPR first derivative spectrum of dppc was recorded using a strong solution in THF. This spectrum

consists of eight broad lines attributable to hyperfine coupling of the unpaired electron with the cobalt nucleus of spin 7/2. DuBois et al. did not observe any

Species	ν <sub>1</sub> /cm <sup>−−1</sup>	r <sub>2</sub> /cm <sup>-1</sup>	v3/cm-1	$v_4/cm^{-1}$	v <sub>5</sub> /cm <sup>-1</sup>	r <sub>6</sub> /cm <sup>-1</sup>	ν <sub>7</sub> /cm <sup>−1</sup>
Ru <sub>s</sub> C(CO) <sub>15</sub>	2104 (w)	2068 (vs)	2034 (s)	2018 (m)	1967 (vw)		
Ru <sub>s</sub> C(CO) <sub>15</sub> +dppc (5 min)	2068 (m)	2044 (s)	2022 (m)	2012 (sh)	1973 (s)	1964 (s)	1738 (w)
$Ru_sC(CO)_{1s} + dppc (2 h)$	2070 (m)	2056 (m)	2045 (s)	2023 (s)	2012 (sh)	1976 (m)	1964 (m)
$Ru_sC(CO)_{1s} + dppc$ (21 h)	2071 (s)	2059 (s)	2036 (s)	2023 (vs)	1998 (s, br)		
Ru <sub>s</sub> C(CO) <sub>13</sub> (µ-dppc) 7 (48 h)	2071 (m)	2056 (m)	2035 (s)	2023 (vs)	1999 (s, br)		
Ru <sub>s</sub> C(CO)13(µ-dppc)+ 7+	2079 (m)	2060 (sh)	2046 (s)	2033 (vs)	2007 (s, br)	2000 (s, br)	
Ru <sub>5</sub> C(CO) <sub>13</sub> (µ-dppf) 4	2072 (m)	2055 (w)	2037 (s)	2024 (vs)	2002 (m)		

Table 6 IR data of Ru<sub>5</sub>C(CO)<sub>15</sub> and dppc-adducts compared with dppf-adducts

signal using a  $10^{-3}$  M solution in toluene at r.t. [21]. Only at lower temperatures is it possible to 'freeze in' the rapid relaxation of the unpaired electron, hence we used liquid nitrogen (77 K) as coolant. It is not clear why a strong solution in an unusual solvent (for EPR) led to the desired result.

An electron paramagnetic resonance spectrum of 7 was recorded to compare it with the ligand spectra (see Table 7 and Fig. 12). The product is clearly paramagnetic and the spectrum slightly different from that obtained for dppc. Since a weaker solution was used, the gain had to be increased and the signal is superimposed on the baseline of the dewar used to cool the sample, hence the unusual 'U' shape. It is not straight forward to interpret because there appears to be a phase change in the centre of the spectrum. However a g-value and the hyperfine coupling constant  $a(^{59}Co)$ could be determined and are also given in Table 7. There is a significant decrease of  $a(^{59}Co)$  when compared to the title ligand, indicating that the unpaired electron is spending less time on the cobaltocene system. A transfer of electron density to the cluster must therefore have occurred, giving more weight to the proposed Zwitterionic equilibria.

# 2.12. Magnetic susceptibility of $[Ru_5C(CO)_{13}\{\mu-Co(C_5H_4P(Ph)_2)_2\}]$ 7

Magnetic susceptibility measurements show 7 to be paramagnetic at all temperatures (Fig. 14). The corrected data were fitted to both a Curie and a Curie– Weiss expression plus a TIP term. The quality of the fit was appreciably better when a small Curie–Weiss constant  $\Theta$  of -0.36 K was included, and the corresponding values of the Curie constant *C* and TIP contributions were 0.68 emu K mol<sup>-1</sup> and 0.0166C, respectively. The value of *C* corresponds to an  $\mu_{eff}$  of 2.33(1) BM at high temperatures. It appears, therefore, that the moment on the cobaltocene/cluster unit is considerably greater than the moment that would arise from a spin triplet state, and that there is a very weak antiferromagnetic coupling between the units. For dppc, a value of  $\mu_{eff} = 1.73$   $\mu_{B} = 2.02 \times 10^{-29}$  V s m was reported [22]—and that is ca. the normal spin only value [28]. The high magnetic moment observed for 7 may result from an orbital contribution due an interaction with the cluster LUMO. This explanation is consistent with the EPR and IR spectroscopic data.

#### 3. Conclusions

When we finally put together the experimental evidence for this group of molecules the picture is complex. The solid-state structures of 3 and 4 may be considered to be a 'snap-shot' of the highly stereochemically non-rigid molecules (Fig. 8) and it is possible to postulate the existence of many structural permutations of the molecules all of similar global energy. Solution analyses have shown that the rate of these structural interconversions is temperature dependent. One might anticipate that the degree of itinerant electronic behaviour and consequent structural distortion is dependent upon the molecular environment; viz. polar media would favour the charge separated species and vice versa. It would therefore be of interest to measure the magnetic susceptibility of 3, 4 and 7 in a highly polar host compound.

We have now instigated a thorough investigation into a wide variety of systems designed to produce similar interactions between clusters and proximal redox-active centres. The study of itinerant electronic behaviour in these systems is a specific goal. Further work in this area may do well to include solvatochromic measurements due to the polar nature of compound 3. Incidentally, it was noticed that compound 3 was more intensely coloured when adsorbed onto silica. Further information may be derived from the electronic spectra if they are obtained at low temperature. Also computer software for deconvolution studies may enhance the resolution. The range of compounds synthesised so far is insufficiently broad to safely draw many conclusions (e.g. the origin of the large  $\mu_{eff}$  in 7), hence we intend to make and study a wide range of similar compounds. Further understanding of the electronic behaviour observed in this area requires a strong partnership be-



Fig. 10. The EPR spectrum of dppc, powder under nitrogen at 77 K, 3000 G sweep width,

tween experiment and theory, and so further elucidation of the electronic properties of these cluster-metallocene compounds should be made on a more firm theoretical footing. It is reasonable to expect novel characteristics and possibly useful properties to be found in such systems.

#### 4. Experimental

All reactions were carried out with the exclusion of air using solvents dried and distilled under an atmosphere of nitrogen. Subsequent work-up of products was achieved without precautions to exclude air. IR spectra were recorded on a Perkin-Elmer 1710 series FTIR instrument in CH<sub>2</sub>Cl<sub>2</sub> using NaCl cells (0.5 mm path length). <sup>1</sup>H-NMR spectra were recorded in CDCl<sub>3</sub> and CD2Cl2 using a Braker AM360 instrument, referenced to internal TMS. Separation of products was accomplished by TLC using plates supplied by Merck, 0.25 mm layer of Kieselgel 60 F254. The clusters  $Ru_6C(CO)_{17}$  and  $Ru_5C(CO)_{15}$  were prepared by the standard literature procedures. The dppf used was purchased from Aldrich and used without further purification. Schlenk-techniques have always been used unless otherwise mentioned.

#### 4.1. Preparation of $[Ru_6C(CO)_{16}{Fe(C_5H_4P(Ph)_2)_2}]$ 2

A total of 100 mg of 1 (0.091 mmol) and 48 mg (0.091 mmol) of dppf were dissolved in 35 ml of THF. The resulting solution was refluxed for 1 h under a nitrogen atmosphere. After cooling to r.t., the solvent was removed in vacuo. Separation of products was achieved by TLC using dichlorornethane:hexane as cluent (3:7 v/v). The major red-brown band 2 was extracted with dichloromethane as the major product (90%) along with a small amount of green 3 (ca. 5%). Elemental analysis of  $C_{51}H_{28}FeO_{16}P_2Ru_6\cdot CH_2Cl_2$  (2) gave C 36.79, H 1.68 (calc. C 36.61, H 1.77%).

#### 4.2. Thermolysis of 2—preparation of $[Ru_6C(CO)_{15}$ { $\mu$ -Fe(C<sub>5</sub>H<sub>4</sub>P(Ph)<sub>2</sub>)<sub>2</sub>] 3

A total of 50 mg of 2 (0.029 mmol) was dissolved in 35 ml of THF. The resulting solution was refluxed for 5 h under a nitrogen atmosphere. After cooling to r.t., the solvent was removed in vacuo. Separation of products was achieved by TLC using dichloromethane: hexane as eluent (1:3 v/v). A red-brown band of unconverted 2 was extracted with dichloromethane (ca. 35%) along with green 3 (ca. 55%) as the major product. Alternatively, refluxing in cyclohexane (35 ml) for 1.5 h gave the following product distribution: 25% 2, 70% 3, 5% 4. Elemental analysis of 3 gave C 37.43, H 1.9 (calc. C 37.32, H 1.78%).

#### 4.3. Thermolysis of 2—preparation of $[Ru_5C(CO)_{13}$ $\{\mu$ -Fe $(C_5H_4P(Ph)_2)_2\}$ ] 4

A total of 50 mg of 2 (0.029 mmol) was refluxed in 35 ml of octane for 3 h under a nitrogen atmosphere. After cooling to r.t., the solvent was removed in vacuo. Separation of products was achieved by TLC using dichloromethane:hexane as eluent (2:3 v/v). A very feint red-brown band of unconverted 2 was extracted with dichloromethane (ca. 1%) along with green 3 (ca. 40%) and bright purple 4 (55%) as the major product.

#### 4.4. Thermolysis of 3—preparation of $[Ru_5C(CO)_{13}$ $[\mu-Fe(C_5H_4P(Ph)_2)_2]$ 4

A total of 25 mg of 2 (0.013 mmol) was refluxed in 35 ml of octane for 2 h under a nitrogen atmosphere. After cooling to r.t., the solvent was removed in vacuo. Separation of products was achieved by TLC using dichloromethane:hexane as eluent (2:3 v/v). A green band of unconverted 3 was extracted with dichloromethane (ca. 20%) and bright pink 4 (75%) as the major product.



Fig. 11. The EPR spectrum of dppc, frozen solution in THF at 77 K, 3000 G sweep width.

# 4.5. Direct synthesis of $[Ru_5C(CO)_{13}{\mu-Fe(C_5H_4 P(Ph)_2)_2}]$ 4

A total of 25 mg of 6 (0.027 mmol) and 15 mg (0.027 mmol) of dppf were dissolved in 15 ml of THF. The resulting solution was stirred for 1 min under a nitrogen atmosphere. Effervescence indicated evolution of CO. After the solvent was removed in vacuo, purple 4 was purified by crystallisation by solvent diffusion using dichloromethane/hexane. Dark purple crystals of 4 were grown overnight and identified as the only product (99%). Elemental analysis of 4 gave C 40.09, H 2.0 (calc. C 39.71, H 1.94%).

## 4.6. Synthesis of 1,1'-Bis(diphenylphosphino)cobaltocene (dppc)

A 12.67 g (70.7 mmol) sample of NaCp DME was dissolved in 100 ml THF and cooled to - 78°C. A total of 15.8 g (13.2 ml, 71.8 mmol, 1.6% excess) chlorodiphenylphosphine, CIPPh2, previously distilled at 145-160°C under vacuum, was added via syringe and septum. The mixture was allowed to warm up to r.t. and stirred for 90 min. The reaction mixture containing the 1-(diphenylphosphino)cyclopentadiene was used immediately. It was assumed that the yield from that reaction was not higher than the 81% given in the literature. A 5.87 ml portion of a 10 M solution of n-butyl lithium in hexane (68.7 mmol, 20% excess) were added to the mixture at - 78°C via syringe. The solution was then allowed to warm up to r.t. and stirred over several days. A brown turbid solution yielded due to the still present NaCl. Again, the reaction mixture

from the previous step was used without further purification and the amounts of reactants were reduced by the literature yield of 95%. A 3,53 g (27.2 mmol) sample of dry cobalt chloride was added at -78°C using a counter stream of nitrogen and a T-working piece. The previously light brown and muddy mixture turned to dark red, even at  $-78^{\circ}$ C. At ambient temperature, the colour darkened and turned to a reddish black after stirring overnight. Heating under reflux for 40 min brought the reaction to an end. THF was replaced by 120 ml of toluene. Filtration through a frit that was improved by adding 2 ml of dry SiO<sub>2</sub> and some glass wool yielded a black solution. The solvent was evaporated on a Schlenk line and a black, non-crystalline product remained. Pure crystals were obtained by either layering a saturated solution in toluene with hexane or by cooling a hot saturated solution in toluene. A solution of the purified product dppc in THF is dark violet. Elemental analysis of the crystallised neutral ligand was in good agreement with the calculated data. Anal. Calc. for C34H28CoP2: C 73.2, H 5.06. Found: C 73.2, H 4.80, N 0%.

#### 4.7. Synthesis of 1,1'-bis(diphenylphosphino)cobaltocenium hexafluorophosphate (dppc<sup>+</sup>)

#### 4.7.1. Oxidation with ferrocenium tetrafluoroborate

All steps of the synthesis of dppc were performed again, stopping with the crude product in toluene. The scale was determined by using 4.957 g (38.18 mmol) CoCl<sub>2</sub>, yielding about 35.35 mmol dppc. Oxidation was achieved using ferrocenium tetrafluoroborate, FeCp<sub>2</sub>+  $BF_4^-$ , which was synthesised by oxidising 6.65 g (35.35

Sample	dppe (powder)	dppc (frozen solution)	7 (frozen solution)
Gain	3×10 <sup>4</sup>	3.2×104	2 × 10 <sup>5</sup>
Time constant	2 s	500 ms	500 ms
Frequency (GHz)	9.35	9,35	9.35
Centre field (G)	3300	3300	3300
Sweep width (G)	3000	3000	1500
Temperature (K)	77	7"	77
Solvent	None	T'';	THF/hexane
Modulation	6.3	63	20.0
g-Value	1.83579, 1.96600	1.99983	2.01544
a(59Co) (G)	Not observable	148.62	146.69

Table 7		
Data for EPR	spectra of dppc and compound 7	

mmol) FeCp2 with 6.88 g (35.35 mmol) AgBF4 in 50 ml THF. The ferrocenium salt was extracted with acetonitrile, thus leaving the side product, silver metal, behind. This solution was added to the reaction mixture together with 7.375 g (45.25 mol) ammonium hexafluorophospate dissolved in a minimum of water as counter-ion. The resulting solution, of dark orange colour, was filtered through a column of silica and eluted first with hexane/Et<sub>2</sub>O to remove neutral species such as ferrocene, then with CH<sub>2</sub>Cl<sub>2</sub> and fnally with CH<sub>3</sub>CN to collect the product. Crystallisation from the dichloromethane fraction by layering with hexane or diethylether failed: a thick black oil was formed. Therefore, the remaining liquid was decanted off and quickly f Itered through paper, yielding orange crystals and some impure product after addition of pentane. The overall yield of dppc+ was very low, due to the instability whilst in solution (ca. 5%).

#### 4.7.2. Oxidation with oxygen

A 1.1 g (1.973 mmol) sample of dppc, the raw product from synthesis, was dissolved in 30 ml THF and an excess of acetic acid (100%) and distilled water was added. Air was sucked through the solution, yielding a very dark yellow solution over a black residue at the bottom of the flask. After 3 h, the solution was filtered. Ammonium hexafluorophosphate (0.386 g. 2.367 mmol, 20% excess) was dissolved in a minimum of distilled water and added to the filtrate. Ethanol (5.64 ml) was added and the solvent volume was then reduced using a roto-evaporator. The yielding yellow oil and brown solid were then chromatographed in a column packed with silica gel, using dichloromethane with 1-2% THF as eluent. A very small amount of yellow crystals were obtained. The 1H-spectrum compared favourably with the chemical slifts given in the literature. DuBois et al. [21] gave  $\delta$  5.36 (t), 5.68 (t, Cp), 7.42 (br s, Ph) ppm in CD<sub>2</sub>CN, which are in good agreement with the following shifts recorded in CDCl, (250 MHz, 298 K): 0 5.36 (m), 5.76 (m), 7.43 (br m) ppm.

The <sup>31</sup>P-spectrum was recorded to ensure that only one product was isolated; for this DuBois et al. [21] gave a single signal in CD<sub>3</sub>CN at  $\delta = 23.09$  ppm. Consistent with this, a signal was observed with the highest intensity at  $\delta = 21.82$ , along with three much smaller peaks at  $\delta$  23.62, 30.07, and 33.59 ppm (CDCl<sub>3</sub>, 101 MHz, 298 K). Those impurities are believed to come from phosphine oxides that could not be prevented in the oxidation step. Interestingly, dppc<sup>+</sup> is a yellow powder that is moderately stable when dry and cooled to  $-18^{\circ}$ C, but which decomposes rapidly even in dry solvents to form a black 'mud'. Elemental analysis of the oxidised ligand also proved to be in good agreement with the calculated data. Anal. Calc. for C<sub>14</sub>H<sub>28</sub>CoF<sub>6</sub>P<sub>3</sub>; C 58.13, H 4.02, Found: C 57.77, H 3.82, N 0%. A + FAB mass spectrum of the oxidised ligand was recorded. Apart from some breakdown peaks in the region m/z 130–190, the most intense peaks were found at m/z 558 (73.8) and 574 (73.3%). The former reflects the molecular ion peak of  $[Co(C_5H_4PPh_2)_2]^+$  with M = 557.49 g mol<sup>-1</sup>, the latter a phosphine oxide where one of the phosphorus atoms is bound to an oxygen atom with M = 573.49 g mol<sup>-1</sup>. The MS data adds weight to the breakdown pathway for the oxidised ligand, as already suspected from the <sup>31</sup>P-NMR spectrum (vide supra).

#### 4.8. Reactions with the hexaruthenium carbido cluster Ru<sub>6</sub>C(CO)<sub>17</sub>

An excess of dppc was dissolved in THF and 200 mg (0.1827 mmol) [Ru<sub>6</sub>C(CO)<sub>17</sub>] I was added using a counter stream of nitrogen at 0°C. A reaction took place, indicated by a small amount of effervescence (Co†). After 30 min at r.t., an IR spectrum was recorded, showing a shifted CO-stretch attributable to the reduced cluster [Ru<sub>6</sub>C(CO)16]<sup>2-</sup>. A 0.100 g (0.3654 mmol) sample of ferrocenium te<sup>+</sup>rafluoroborate in 5 ml THF, twice the stoichiometric amount of cluster, was added with a syringe. A slight colour change to reddish occurred overnight. Column chromatography on silica



Fig. 12. The EPR spectrum of 7 in THF/hexane at 77 K, sweep width 1500 G

gel ... applied on the mixture, initially using dichloromethane:hexane (50:50 v/v), then acctone:hexane (50:50 v/v), yielding a yellowish dichloromethane-soluble fraction (A) and purple/pink acetone-soluble fraction (B). Both solutions were reduced in vacuo under a normal atmosphere. Fraction (A) contained a mixture of unteacted starting materials, ferrocene and dppf<sup>+</sup> and was dicarded.

Fraction (B) was separated by TLC on silica gel using hexane:dichioromethane:ethyl acetate:acetone (50:30:10:10 v/v) as mobile phase. One major and two minor bands were detected. Three bands yielded: minor (B1), purple/pink in CH<sub>2</sub>Cl<sub>2</sub>, IR recorded; major (B2) 7<sup>+</sup>, purple in CH<sub>2</sub>Cl<sub>2</sub>, IR and <sup>31</sup>P-NMR at different temperatures recorded; minor (B3), brown-purple, difficult to extract from SiO<sub>2</sub>, but IR recorded.

#### 4.9. Reaction with $[Ru_5C(CO)_{13}\{\mu-Co(C_5H_4P(Ph)_2)_2\}]$ 7

A total of 72 mg (0.0772 mmol) Ru<sub>5</sub>C(CO)<sub>15</sub> and 43 mg (equimolar) dppc were stirred in THF at r.t. IR specta were taken after 5 min, 2 h and 48 h. The colour changed from brown via a reddish purple to an intense, dark red. Crystallisation with THF/hexane layering yielded pure, but small crystals. Anal. Calc. for (7)  $C_{48}H_{28}COO_{15}P_2Ru_5$ : C 46.06, H 1.97. Found: C 40.13, H 1.90, N 0%.

Spectroscopic data for **2**: IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu_{CO}$  cm<sup>-1</sup>: 2083m, 2056s, 2043sh, 2030s, 1980m.br, 1830w.br. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 223 K):  $\delta$  7.35 (br.m, 20H), 4.15 (br.m, 8H) ppm.

Spectroscopic data for 3: IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu_{co}$  cm<sup>-1</sup>: 2070s, 2034vs, 2024vs, 2012s, 1994m, 1971w.br, 1961w.br, 1853w.br, 1816w.br. <sup>31</sup>P-NMR (CDCl<sub>3</sub>, 298 K.): δ 43.78 (br.s) ppm. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 298 K): δ
 7.58 (br.m, 20H), 4.12 (br.m, 8H) ppm.

Spectroscopic data for 4: IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu_{CO}$  cm<sup>-1</sup>: 2072s, 2055w, 2037s, 2024vs, 2007s.br. <sup>31</sup>P-NMR (CD<sub>2</sub>Cl<sub>2</sub>, 218 K):  $\delta$  29.97 (s, IP), 26.59 (s, IP) ppm. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 223 K):  $\delta$  7.79 (m, 2H), 7.51 (m, 20H), 7.19 (m, 2H), 4.98 (br.s, 1H), 4.29 (br.s, 1H), 4.22 (br.s, 1H), 4.15 (br.s, 2H), 3.76 (br.s, 1H), 3.41 (br.s, 2H) ppn.

Spectroscopic data for 7: IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu_{CO}$  cm<sup>-1</sup>: 2071 m, 2056m, 2035s, 2023vs, l 999m.br. + FAB MS showed the molecular ion peak corresponding to Ru<sub>5</sub>C(CO)<sub>13</sub>{ $\mu$ -Co[C<sub>5</sub>H<sub>3</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sup>2</sup> with M = 1438.98g mol<sup>-1</sup> around m/z 1440. The resolution of this spectrum was poor but peaks corresponding to the elimination of up to seven CO molecules could be recognised around m/z 1413, 1383, 1357, 1328, 1302, 1272, 1246. As an additional feature, the molecular ion peak of the ligand dppc could be identified.

Spectroscopic data for 7<sup>+</sup>: IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu_{CO}$  cm<sup>-1</sup>: 2079m, 2060sh, 2046s, 2033vs, 2007m.br, 2000m.br. <sup>31</sup>P-NMR (CD<sub>2</sub>Cl<sub>2</sub>, 218 K) [BF<sub>4</sub><sup>-</sup> counter ion]:  $\delta$  23.71 (s, 1P), 29.20 (s, 1P) ppm. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 298 K):  $\delta$ 7.50 (br.m, 20H), 5.63 (br.m, 8H) ppm. FAB + m/z  $M^+$  = 1437 emu (calc. 1438.98). <sup>1</sup>H-NMR (CD<sub>3</sub>)<sub>2</sub>CO at 298 K: 7.70 (br.m, 20H), 6.10 (br.m, 2H), 5.92 (br.m, 2H), 5.74 (br.m, 2H) and 5.66 (br.m, 2H) ppm.

Crystal data for 3:  $C_{s0}H_{28}FeO_{15}P_2Ru_6 \cdot 2CH_2CI_2$ , M = 1643.94, monoclinic, space group  $P2_1/n$  with a =17.280(3), b = 18.488(4), c = 17.359(3) Å,  $\beta = 92.09(3)^\circ$ , V = 5542(2) Å<sup>3</sup>,  $D_{culc.} = 2.101$  g cm<sup>-3</sup>, Z = 4,  $\mu = 2.512$ mm<sup>-1</sup>, T = 150.0(2) K. Diffraction amplitudes were acquired using a Stöe-Stadi-4 four circle diffractometer, graphite-monochromated Mo-K<sub>x</sub> X-radiation and an Oxford Cryosystems low-temperature device [30]. Of



Fig. 13. A qualitative MO diagram for dppc+ [33].

8872 reflections collected to  $2\theta_{max} = 50^\circ$ , 7213 were unique ( $R_{int} = 0.064$ ). The structure was solved by automatic direct methods (Ru) [31] and developed through iterative cycles of least-squares refinement and difference Fourier synthesis. Dichloromethane solvate molecules occupy channels between molecules of 1 and modelling of their substantial disorder was successful. Anisotropic refinement was allowed for Ru, Fe, P and O atoms and non-solvent H atoms were included in fixed, calculated positions [32]. At final convergence with *R* [*F* > 4σ(*F*)] = 0.074, *wR*<sub>2</sub> [*F*<sup>2</sup>, 7161 data] = 0.1851, *S* = 1.055, for 465 refined parameters and the final Δ*F* synthesis showed no feature outside the range + 1.44 to - 1.02 e Å<sup>-3</sup>.

Crystal data for 4:  $C_{48}H_{28}FeO_{13}P_2Ru_5$ , M = 1435.84, orthorhombic, space group *Pbca* with a = 16.222(3), b = 21.072(4), c = 26.983(5) Å, V = 9224(3) Å<sup>3</sup>,  $D_{cubc.} =$ 2.068 g cm<sup>-3</sup>, Z = 8,  $\mu = 2.038$  mm<sup>-1</sup>, T = 150.0(2)K. Diffraction amplitudes were acquired using a StoeStadi-4 four circle diffractometer, graphite-monochromated Mo-K<sub>x</sub> X-radiation and an Oxford Cryosystems low-temperature device [30]. Of 6314 reflections collected to  $2\theta_{max} = 50^{\circ}$ , 6314 were unique. The structure was solved by automatic direct methods (Ru) [31] and developed through iterative cycles of least-squares refinement and difference Fourier synthesis. Anisotropic refinement was allowed all non-H atoms and H atoms were placed in fixed, calculated positions [32]. At final convergence with  $R [F > 4\sigma(F)] = 0.059$ ,  $wR_2 [F^2, 6172$ data] = 0.1712, S = 1.152, for 624 refined parameters and the final  $\Delta F$  synthesis showed no feature outside the range  $\pm 0.84$  to -1.01 e Å<sup>-3</sup>.

Electrochemical experiments were carried out using a DSL 286-D PC with General Purpose Electochemical System (GPES) Version 3 software coupled to an Autolab system containing a PSTAT 10 potentiostat. A conventional three electrode cell was employed with Pt counter and micro-working electrodes and Ag[AgCl



Fig. 14. Variation of molar magnetic susceptibility, z, of 7 with temperature. Superimposed on the data points is a line of best fit utilising the Curie-Weiss expression.

reference electrode against which the  $Fc/Fc^+$  couple was measured at +0.55 V. Coulometric studies employed a three electrode H-type cell with Pt basket working electrode. All electrochemical experiments were performed under an atmosphere of argon.

Magnetic susceptibility measurements were performed on powder samples with a SQUID magnetometer (Quantum Design, model MPMS2) at temperatures between 1.8 and 310 K in an applied magnetic field of 0.1 T. The data were corrected for the response of the sample holder and the diamagnetic contributions of all atoms [18].

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#### References

- C. Kollmar, M. Couty, O. Kahn, J. Am. Chem. Soc. 113 (1991) 7994.
- [2] (a) K.M. Chi, J.C. Calabrese, W.M. Reiff, J.S. Millar, Organometallics 10 (1991) 668. (b) J.S. Millar, A.J. Epstein, Angew.Chem. Int. Ed. Engl. 33 (1994) 385.
- [3] R.W. Wagner, P.A. Brown, T.E. Johnson, J.S. Lindsey, J. Chem. Soc. Chem. Comm. (1991) 1463.
- [4] E.C. Constable, Angew. Chem. Int. Ed. Engl. 30 (1991) 407.
- [5] P.D. Beer, Z. Chen, M.G.B. Drew, A.J. Pilgrim, Inorg. Chim. Acta. 225 (1994) 137.
- [6] (a) I.R. Butler, in: E.W.Abel (Ed.), R. Soc. Chem. Spec. Per. Rep., Organometallic Chemistry 21 (1992) 338. (b) N.E. Sharp, M. Petersson, K. Edstrom, J. Electroanal. Chem. 109 (1980) 271. (c) N.G. Connelly, W.E. Geiger, Adv. Organomet. Chem. 23 (1984) 1.
- [7] (a) N. Rosch, L. Ackermann, G. Pacchioni, B.I. Dunlap, J. Chem. Phys. 95 (1991) 7005. (b) I.H. Williams, D. Spangler, D.A. Femec, G.M. Maggiora, R.L. Schowen, J. Am. Chem. Soc.

102 (1980) 6621. (c) V.G. Albano, P. Chini, G. Ciani, M. Sansoni, D. Strumolo, H. Heaton, S. Martinengo, J. Am. Chem. Soc. 98 (1976) 5027.

- [8] D.C. Johnson, P.P. Edwards, R.E. Benfield, W.J.H. Nelson, M.D. Vargas, Nature 314 (1985) 231.
- [9] (a) L.F. Dahl, W.L. Olsen, A.M. Stacy, J. Am. Chem. Soc. 108 (1986) 7646. (b) L.F. Dahl, W.L. Olsen, J. Am. Chem. Soc. 108 (1986) 7657. (c) L.F. Dahl, L.R. Byers, V.A. Uchtman, J. Am. Chem. Soc. 103 (1981) 1942. (d) A.J. Blake, A. Harrison, B.F.G. Johnson, E.J.L. McInnes, S. Parsons, D.S. Shephard, L.J. Yellowlees, Organometallics 14 (1995) 3160. (e) B.F.G. Johnson, J. Lewis, I.G. Williams, J. Chem. Soc. A (1970) 901.
- [10] J.J. Schneider, R. Goddard, C. Kruger, S. Werner, B. Metz, Chem. Ber. 124 (1991) 301.
- For examples see: (a) T.M. Millar, K.J. Ahmed, M.S. Wrighton, Inorg. Chem. 28 (1989) 2347. (b) C.E. Housecroft, S.O. Owen, P.R. Raithby, B.A.M. Shaykh, Organometallics 9 (1990) 1617.
   (c) I.R. Butler, W.R. Cullen, T.J. Kim, S.J. Rettig, J. Trotter, Organometallics 4 (1985) 972. (d) D.A. Clemente, G. Pillioni, B. Corain, B. Longato, M. Tiripiechio-Camellini, Inorg. Chim. Acta 115 (1986) L9.
- [12] (a) S.M. Draper, C.E. Housecroft, A.L. Rheingold, J. Organomet. Chem. 435 (1992) 9. (b) S.T. Chacon, W.R. Cullen, M.I. Bruce, O. Shawkataly, F.W.B. Einstein, R.H. Jones, A.C. Willis, Can. J. Chem. 68 (1990) 2001. (c) A. Togni, T. Hayashi (Eds.), Ferrocenes, VCH, Germany, 1995, Ch. 1. (d) I.D. Salter, S.A. Williams, T. Adatia, Polyhedron 14 (1995) 2803. (c) I.D. Salter, V. Sik, S.A. Williams, T. Adatia, J. Chem. Soc. Dalton Trans. (1996) 643.
- [13] B.P.Gracey, J. Evans, A.G. Jones, M. Webster, Acta.Crystallogr. C43 (1987) 2286.
- [14] R.M. Churchill, R.A. Lashewycz, J.R. Shapeley, S.I. Richter, Inorg. Chem. 19 (1980) 1277.
- [15] M.C.B. Colbert, S.L. Ingham, J. Lewis, N.J. Long, P.R. Raithby, J. Chem. Soc. Dalton. Trans. (1994) 2215.
- [16] S.R. Drake, B.F.G. Johnson, J. Lewis J. Chem. Soc. Dalton Trans. (1989) 243.
- [17] (a) R. Prins, F.J. Reinders, J. Am. Chem. Soc. 91 (1969) 4929.
  (b) D.F. Evans, J. Chem. Soc. (1959) 2003.
- [18] E. König, in: K.H. Hellwege (Ed.), Landholt-Bornstein, New Ser., Group II Atomic and Molecular Physics, vol. 2, Springer, Berlin, 1966.
- [19] B.F.G. Johnson, J. Lewis, J.N. Nicholls, et al., J. Chem. Soc. Dalton Trans. (1983) 277.
- [20] A.W. Rudie, D.W. Lichtenberg, M.L. Katcher, A. Davison, Inorg. Chem. 17 (1978) 2859.
- [21] D.L. DuBois, C.W. Eigenbrot Jr., R.C. Haltiwanger, A. Miedaner, J.C. Smart, Organometallics 5 (1986) 1405.
- [22] I.M. Lorkovic, M.S. Wrighton, W.M. Davis, J. Am. Chem. Soc. 116 (1994) 6220.
- [23] See for example: (a) M.R. Churchill, R.A. Lashewycz, Inorg. Chem. 17 (1978) 1950. (b) M.R. Churchill, R.A. Lashewycz, J.R. Shapley, S.I. Richter, Inorg. Chem. 19 (1980) 1277. (c) B.P. Gracey, J. Evans, A.G. Jones, M. Webster, Acta Crystallogr. C43 (1987) 2286.
- [24] A.J. Blake, A. Harrison, B.F.G. Johnson, E.J.L. McInnes, S. Parsons, D.S. Shephard, L.J. Yellowlees, Organometallics 14 (1995) 3160.
- [25] Ch. Elschenbroich et al., University of Marburg, Germany.
- [26] E.A.V. Ebsworth, D.W.H. Rankin, S. Cradock, Structural Methods in Inorganic Chemistry, 2nd ed., Blackwell, Oxford, 1991, p. 97.
- [27] M.R. Churchill, R.A. Lashewycz, J.R. Shapley, S.I. Richter, Inorg. Chem. 19 (1980) 1277.
- [28] J.S. Miller, A.J. Epstein, Angew. Chem. Int. Ed. Engl. 33 (1994) 385.

136

- [29] (a) Ch. Elschenbroich, A. Satzer, Organometallchemie-eine kurze Einfahrung, 3rd ed., Teubner, Stuttgart, 1993, p. 278; also see Section 1.20 for further examples. (b) Y.S. Sohn, D.N. Hendrickson, H.B. Gray, Inorg. Chem. 10 (1970) 3233. (c) D.N. Hendrickson, D.M. Duggan, Inorg. Chem. 14 (1975) 955.
- [30] J. Cosier, A.M. Glazer, J. Appl. Cryst. 19 (1986) 105.
- [31] G.M. Sheldrick, SHELXS-86, Acta Crystallogr. A46 (1990) 467.
- [32] G.M. Sheldrick, SHELXL-93, University of Göttingen, Germany.
- [33] J.H. Ammeter, J.D. Swalen, J. Chem. Phys. 57 (1972) 678.