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Contribution from the Laboratoires de Chimie des Organométalliques et de Chimie du Solide et Inorganique Moléculaire and the Centre de Mesures Physiques, Université de Rennes, Campus de Beaulieu, 35042 Rennes Cedex, France

Synthesis of Novel Halo-Bridged Trinuclear Ruthenium-Iron Derivatives. X-ray Structure of $FeRu_2(\mu\text{-}Cl)_2(CO)_8(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)_2$

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Reaction of $RuCl_2(L)C_6H_6$ (**1**) (L = $P(OMe)_3$, PPh_3, PMe_2Ph, PMe_3, $Ph_2PC{\equiv}C\text{-}t\text{-}Bu$) with $Fe_2(CO)_9$ yields trinuclear complexes $Ru_3(CO)_{10}L_2$ (**2**), $FeRu_2(CO)_{10}L_2$ (**3**), and $RuFe_2(CO)_{11}L$ (**4**) which has two carbonyls bridging the equivalent iron atoms and, as the major product, the novel derivative $FeRu_2(\mu\text{-}Cl)_2(CO)_8L_2$ (**5**) resulting from partial dehalogenation. All these compounds have the phosphorus groups selectively bonded to the ruthenium atoms. The compound $FeRu_2(\mu\text{-}Cl)_2(CO)_8(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)_2$ (**5e**) crystallizes in space group $P2_1/c$ with cell dimensions a = 12.103 (1) Å, b = 21.618 (7) Å, c = 17.949 (5) Å, β = 97.873 (27)°, and Z = 4. Refinement based on 3520 observed diffractometer data converged at $R = R_w = 0.083$. Each phosphorus atom is coordinated to one ruthenium atom in a position trans to the Fe–Ru bonds which are equivalent [Fe–Ru(1) = 2.808 (3) Å and Fe–Ru(2) = 2.809 (3) Å]. The Ru–Fe–Ru angle is 69.07 (4)°. The ruthenium atoms are bridged by two chloro groups and are maintained at a distance of 3.185 (2) Å. The relative positions of the phosphinoacetylene groups destroy the C_{2v} symmetry.

Introduction

Recently transition-metal cluster compounds have attracted interest as possible precursors of a new class of homogeneous catalysts:[2] they are able either to generate new active mononuclear species by cleavage of metal–metal bonds or to promote reactions by cooperative interaction of several metal centers. Polymetallic carbonyl derivatives have potential as catalysts for the hydrogenation of carbon monoxide[2,3] or the water–gas shift reaction. In the latter case activity is enhanced by mixing ruthenium and iron carbonyl complexes as compared to each of these parent complexes.[4]

In spite of their interest only a few mixed iron–ruthenium cluster compounds have been characterized,[5] most of which were obtained by complete dehalogenation of Ru(II) or Ru(III) derivatives[6] or by reaction of cluster carbonyl compounds with organometallic anions.[5]

We report here a new type of mixed ruthenium–iron trimetallic complex containing the $FeRu_2(\mu\text{-}Cl)_2$ moiety which is built by bringing together mononuclear fragments resulting from the partial dehalogenation of $RuCl_2(PR_3)$(arene) derivatives by $Fe_2(CO)_9$. The X-ray structure of $FeRu_2(\mu\text{-}Cl)_2(CO)_8(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)_2$ establishes an Ru–Fe–Ru triangular arrangement with two bridging chloro groups.

Experimental Section

Synthesis. General Procedures. The derivatives **1a–e** were synthesized from $[RuCl_2(arene)]_2$ according to the described procedure.[7] In a typical reaction 0.5 g of **1** and 2 equiv of $Fe_2(CO)_9$ in 40 mL of benzene or toluene were stirred at room temperature for 24 h. After filtration, solvent was removed from the brown solution under vacuum, and the products were separated by silica gel thick-layer chromatography (eluant hexane–ether). Four compounds **2** (yellow), **3** (pink), **4** (violet), and the major product **5** (orange) were successively isolated. The complexes were crystallized from mixtures of hexane and of dichloromethane, and they were air stable in the solid state.

Derivatives $Ru_3(CO)_{10}L_2$ (2a and 2d). 2a (L = $P(OMe)_3$): 11% yield; mp 93–94 °C; IR (Nujol) 2084, 2026, 2005, 1997, 1988, 1972, 1942 cm^{-1}; mass spectrum m/e (M ($C_{16}H_{18}O_{16}P_2Ru_3$)) 835.718 (calcd 835.721) (M – CO) 807, (M – 2CO) 779, (M – 3CO) 751, (M – 4CO) 723.740 (calcd 723.741), (M – 5CO) 695, (M – 6CO) 667, (M – 7CO) 639. Anal. Calcd for $C_{16}H_{18}O_{16}P_2Ru_3$: C, 23.02; H, 2.16; Ru, 36.46. Found: C, 23.05; H, 2.05; Ru, 36.25.

2d (L = PMe_3): 4% yield; mp 140–150 °C dec; IR (Nujol) 2022, 2012, 1988, 1974, 1954, 1938 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.60 (d, PMe, $^2J_{P-H}$ = 10 Hz).

Derivatives $FeRu_2(CO)_{10}L_2$ (3a–3d). 3a (L = $P(OMe)_3$): 9.5% yield; mp 123–125 °C; IR (Nujol) 2080, 2020, 2005, 1995, 1975, 1960, 1890 cm^{-1}; mass spectrum m/e (M ($C_{16}H_{18}O_{16}P_2FeRu_2$)) 789.7516 (calcd 789.7514), (M – 2CO) 733, (M – 3CO) 705, (M – 4CO) 677, (M – 5CO) 645, (M – 6CO) 621.7825 (calcd 621.7822), (M – 7CO) 593, (M – 8CO) 565, (M – 9CO) 537, (M – 10CO) 505. Anal. Calcd for $C_{16}H_{18}O_{16}P_2FeRu_2$: C, 24.42; H, 2.29. Found: C, 24.54; H, 2.37.

3b (L = PPh_3): 10.5% yield; mp 155–160 °C; IR (Nujol) 2080, 2015, 1995, 1985, 1945, 1940 cm^{-1}.

3c (L = PMe_2Ph): 5% yield; mp 158–161 °C dec; IR (Nujol) 2075, 2020, 1990, 1980, 1970, 1955, 1928 cm^{-1}. Anal. Calcd for $C_{26}H_{22}O_{10}P_2FeRu_2$: C, 38.32; H, 2.70; P, 7.61; Fe, 6.87. Found: C, 38.52; H, 2.61; P, 7.07; Fe, 6.93.

3d (L = PMe_3): 11% yield; mp 148–150 °C; IR (Nujol) 2078, 2005, 1995, 1975, 1960, 1936 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.61 (d, $^2J_{P-H}$ = 10.0 Hz).

Derivatives $RuFe_2(\mu\text{-}CO)_2(CO)_9L$ (4a–4d). 4a (L = $P(OMe)_3$): 5% yield; mp 97–99 °C; IR (Nujol) ν(C≡O) 2100, 2040, 2025, 2010, 1990, 1976, 1965, 1942, $\nu(\mu\text{-}CO)$ 1837, 1805 cm^{-1}; mass spectrum m/e (M ($C_{14}H_9O_{14}PFe_2Ru$)) 645.748 (calcd 645.747), (M – CO) 617, (M – 2CO) 589, (M – 3CO) 561, (M – 4CO) 533, (M – 5CO) 505, (M – 6CO) 477, (M – 8CO) 449, (M – 8CO) 421, (M – 9CO) 393, (M – 10CO) 365, (M – 11CO) 337, (Ru(CO)P(OMe)$_3$) 254.226. Anal. Calcd for $C_{14}H_9O_{14}PFe_2Ru$: C, 26.04; H, 1.39. Found: C, 26.09; H, 1.41.

4b (L = PPh_3): 4% yield; mp 136–140 °C; IR (Nujol) ν(CO) 2088, 2035, 2014, 1998, 1987, 1980, $\nu(\mu\text{-}CO)$ 1842, 1802 cm^{-1}.

4c (L = PMe_2Ph): 20% yield; mp 134–136 °C; IR (Nujol) ν(CO) 2090, 2025, 2000, 1990, 1968, 1955, $\nu(\mu\text{-}CO)$ 1837, 1795 cm^{-1}. Anal. Calcd for $C_{19}H_{11}O_{11}PFe_2Ru$: C, 34.59; H, 1.66; P, 4.70; Fe, 16.99. Found: C, 34.55; H, 1.73; P, 4.74; Fe, 16.99.

4d (L = PMe_3): 9% yield; mp 148–150 °C[; IR (Nujol) ν(C≡O) 2090, 2025, 2005, 1980, 1973, 1967, 1958, $\nu(\mu\text{-}CO)$ 1837, 1800 cm^{-1}; mass spectrum m/e (M ($C_{14}H_9O_{11}PFe_2Ru$)) 597.763 (calcd 597.762), (M – CO) 569, (M – 2CO) 541, (M – 3CO) 513, (M – 4CO) 485, (M – 5CO) 457, (M – 6CO) 429, (M – 7CO) 401, (M – 8CO) 373.8028 (calcd 373.8031), (M – 9CO) 345, (M – 10CO) 317, (M – 11CO) 289; ^{1}H NMR ($CDCl_3$) δ 1.86 (d, $^2J_{P-H}$ = 9 Hz). Anal. Calcd for $C_{14}H_9O_{11}PFe_2Ru$: C, 28.09; H, 1.50; P, 5.18; Ru, 16.88. Found: C, 27.30; H, 1.78; P, 5.35; Ru, 16.89.

Derivatives $FeRu_2(\mu\text{-}Cl)_2(CO)_8L_2$ (5a–5e). 5a (L = $P(OMe)_3$): 19% yield; mp 114–116 °C; IR (Nujol) 2070, 2040, 1995, 1987, 1982, 1960, 1952, 1934 cm^{-1}; mass spectrum m/e (M – 4CO) 691, (M – 5CO ($C_9H_{18}Cl_2O_9P_2FeRu_2$)) 663.725 (calcd 663.726), (M – 6CO) 635, (M – 7CO) 607, (M – 8CO) 579. Anal. Calcd for $C_{14}H_{18}Cl_2O_{14}P_2FeRu_2$: C, 20.97; H, 2.24; Cl, 8.86; P, 7.74; Fe, 6.99;

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(2) (a) Muetterties, E. L. *Bull. Soc. Chim. Belg.* **1976**, *85*, 451. (b) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479.

(3) Daroda, R. J.; Blackborow, J. R.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1980**, 1098 and 1101.

(4) Ford, P. C.; Rinker, R. G.; Ungerman, C.; Laine, R. M.; Landis, V.; Moya, S. A. *J. Am. Chem. Soc.* **1978**, *100*, 4595. Ungermann, C.; Landis, V.; Moya, S. A.; Cohen, H.; Walker, H.; Pearson, R. G.; Rinker, R. G.; Ford, P. C. *Ibid.* **1979**, *101*, 5922. Laine, R. M. *Ibid.* **1978**, *100*, 6451.

(5) Gladfelter, W. L.; Geoffroy, G. L. *Adv. Organomet. Chem.* **1980**, *18*, 207 and references cited therein.

(6) Yawney, D. B. W.; Stone, F. G. A. *J. Chem. Soc. A* **1969**, 502.

(7) Zelonka, R. A.; Baird, M. C. *Can. J. Chem.* **1972**, *50*, 3063.

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Table I. Relevant Crystallographic Data

compd	$Ru_2FeCl_2(CO)_8(Ph_2PCC\text{-}t\text{-}Bu)_2$
formula	$Ru_2FeCl_2P_2O_8C_{44}H_{38}$
fw	1085.628
a	12.103 (1) Å
b	21.618 (7) Å
c	17.949 (5) Å
β	97.87 (3)°
V	4652 Å^3
Z	4
D(calcd)	1.55 g cm^{-3}
μ	11.67 cm^{-1}
space group	$P2_1/c$
cryst dimens	0.10 × 0.12 × 0.26 mm
cryst shape	monoclinic prism
temp	20 °C
raidation	Mo K$\bar{\alpha}$
monochromator	graphite
scan angle	$(1.00 + 0.35 \tan \theta)°$
max scan time	80 s
receiving aperture	$(2.00 + 0.35 \tan \theta)$ mm
cryst counter dist	173 mm
2θ limits	2–56°
no. of refined variables	645
no. of unique data used	3520
$R = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert$	0.083
$R_w = (\Sigma\lvert\Delta F\rvert^2/\Sigma w\lvert F_o\rvert^2)^{1/2}$	0.083

Ru, 25.21. Found: C, 21.65; H, 2.32; Cl, 8.81; P, 7.83; Fe, 7.00; Ru, 23.27.

5b (L = PPh$_3$). Alternatively this product was isolated by successive crystallizations in mixtures of hexane–dichloromethane: 40% yield; mp 195–198 °C; IR (Nujol) 2060, 2028, 1993, 1980, 1975, 1963, 1948 cm^{-1}; ^{31}P NMR (CDCl$_3$) δ 21.79 (s).

5c (L = PMe$_2$Ph): 10% yield; IR (Nujol) 2058, 2025, 1982, 1973, 1960, 1950, 1937, 1925 cm^{-1}. Anal. Calcd for $C_{24}H_{22}Cl_2O_8P_2FeRu_2$: C, 34.74; H, 2.65; Fe, 6.75. Found: C, 34.92; H, 2.63; Fe, 6.46.

5d (L = PMe$_3$): 33% yield; mp 114–115 °C; IR (Nujol) 2065, 2027, 1995, 1984, 1975, 1955, 1928, 1920 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.60 (d, $^2J_{P\text{-}H}$ = 10 Hz). Anal. Calcd for $C_{14}H_{18}Cl_2O_8P_2FeRu_2$: C, 23.83; H, 2.55; Cl, 10.07; P, 8.79; Fe, 7.94. Found: C, 24.13; H, 2.70; Cl, 10.00; P, 8.92; Fe, 7.91.

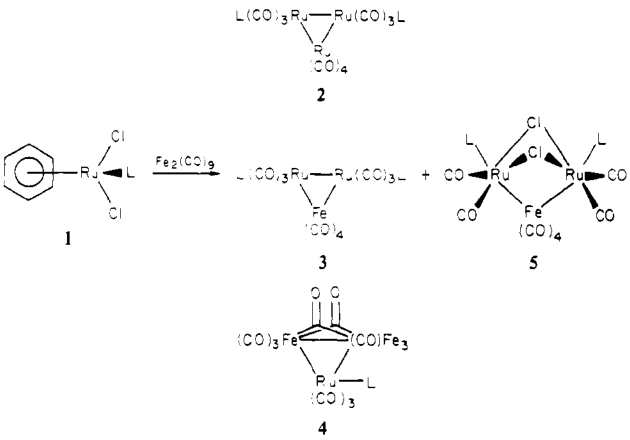
5e (L = Ph$_2$PC≡C-*t*-Bu): 30% yield; mp 183–184 °C; IR (Nujol) ν(C≡C) 2210, 2170, ν(CO) 2065, 2030, 2005, 1980, 1978, 1962, 1947 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.70 (m, C$_6$H$_5$), 1.30 (s, CMe$_3$). Anal. Calcd for $C_{44}H_{38}Cl_2O_8P_2FeRu_2$: C, 48.60; H, 3.50; Cl, 6.54; P, 5.71; Fe, 5.16; Ru, 18.01. Found: C, 48.59; H, 3.80; Cl, 6.80; P, 5.68; Fe, 5.11; Ru, 18.29. [**1e** was obtained according to the general procedure:[7] 95% mp 164–165 °C; IR (Nujol) ν(C≡C) 2215, 2175 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.93 (s, C$_6$H$_6$), 1.50 (s, *t*-Bu).

Derivative FeRu$_2$(μ-I)$_2$(CO)$_8$(P(OMe)$_3$)$_2$ (9): 17% yield; mp 103–105 °C; IR (Nujol) ν(CO) 2065, 2035, 1995, 1987, 1948, 1938 cm^{-1}; mass spectrum m/e (M – Fe(CO)$_4$ ($C_{10}H_{18}O_{10}P_2I_2Ru_2$)) 817.653 (calcd 817.655), (M – Fe(CO)$_5$) 789, (M – Fe(CO)$_6$) 761, (M – Fe(CO)$_7$) 733, (M – Fe(CO)$_8$) 705, (Fe(CO)$_5$) 196.

Collection and Reduction of X-ray Data. A crystal of the title compound, FeRu$_2$(μ-Cl$_2$)(CO)$_8$(Ph$_2$PC≡C-*t*-Bu)$_2$ (**5e**), of approximate dimensions 0.10 × 0.12 × 0.26 mm was mounted on a glass fiber. Preliminary film data showed that the crystal belonged to the monoclinic system with extinctions (*h*0*l*, *l* even; 0*k*0; *k* even) characteristic of the centrosymmetric space group $P2_1/c$. Accurate cell parameters were obtained by a least-squares analysis of 37 carefully centered reflections chosen from diverse regions of reciprocal space. Table I gives the pertinent crystal data and all the details of data collection.

Intensity data were collected with use of the $\omega/2\theta$ method on a Nonius CAD 4 automated diffractometer using Mo Kα radiation (λ = 0.71069 Å). The scan range indicated in Table I was increased by 25% at each end for background measurements, and the scan speed was determined by the relationship $\sigma(I)/I_{\text{net}} < 0.01$. All of the 3520 independent reflections measured having $F_o^2 > \sigma(F_o^2)$ were used in the structure solution and refinement. Due to the relatively small crystal size and less than optimum diffracting properties, a large number of relatively weak reflections were measured. Because of the number of atoms in the molecule (59 nonhydrogen atoms) and consequently a large number of parameter to refine, it was felt advisable to make use of all intensity data available. The data were corrected for Lorentz and polarization effects with use of the program MAXE.[8] No correction for absorption was deemed necessary because of the small size of the crystal and the small linear absorption coefficient. Moreover a check of intensity variations via a ψ scan of several equivalent reflections showed no significant variations in intensity. Three standard reflections monitored every 100 min of X-ray exposure showed no significant changes in intensity throughout the course of data collection.

Scheme I



L = P(OMe)$_3$ (a); PPh$_3$ (b); PMe$_2$Ph (c); PMe$_3$ (d); Ph$_2$PC≡C-*t*-Bu (e)

Solution and Refinement of the Structure. The positions of the heaviest atoms (Ru, Fe, Cl, P) were found with the aid of the program MULTAN[9] in the most probable set and confirmed from the examination of the Patterson function. The positions of all the remaining nonhydrogen atoms were located from a three-dimensional electron density difference map. Atomic scattering factors were taken from Moore's[10] tabulation, and anomalous dispersion terms were included in the calculation of Fe.[11] The model was initially refined, with use of a local version of SFLS-5,[12] by full-matrix least-squares techniques with isotropic thermal parameters for all nonhydrogen atoms and then blocked into three molecular fragments, each of which was refined by a full-matrix least-squares methods with anisotropic thermal parameters to an R value of 0.088. At this point a Fourier difference map, calculated with use of only those reflections for which $(\sin \theta)/\lambda < 0.3$ Å^{-1} showed the positions of all the hydrogen atoms. The hydrogen atoms were initially entered as fixed contributions in idealized positions with isotropic thermal parameters of 4.0 Å^2. Several further cycles of refinement of all nonhydrogen atom parameters failed to reduce, to any significant degree, the R value because of the relatively high standard deviations in F_{obsd}. However, on use of a weighting scheme based on the magnitude of $\lvert F_{\text{obsd}}\rvert$, the refinement finally converged to R = 0.083. The weighting scheme used was such that for the majority of the reflections w = 1, and no correlation existed between F_o and $w(\lvert F_o\rvert - \lvert F_c\rvert)^2$.

No significant peaks remained on a final Fourier difference map, and the average variation of all the nonhydrogen atom parameters was 0.18 esd with the largest variation occurring for the atomic parameters of the atoms in the tertiary butyl group. Table II lists the atomic parameters for the nonhydrogen atoms with their esd's. Bond distances and angles are given in Tables III and IV.

Results and Discussion

Synthetic Aspects. The derivatives RuCl$_2$(L)(C$_6$H$_6$) (**1**) readily available via reaction of the phosphine L with [RuCl$_2$(C$_6$H$_6$)]$_2$[7] react with Fe$_2$(CO)$_9$ in benzene or dichloromethane at ordinary temperature over 24 h to give a mixture of trinuclear complexes separable by silica gel thick-layer

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(8) Le Marouille, J. Y. "Program Maxe et Fourier", Thèse de Doctorat (3rd cycle), Université de Rennes, 1972.

(9) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A127*, 368.

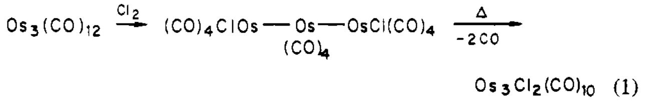
(10) Moore, F. H. *Acta Crystallogr.* **1963**, *16*, 1169.

(11) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4.

(12) Prewitt, C. K. Report ORNL-TM-305; Oak Ridge National Laboratory: Oak Ridge, TN, 1966.

chromatography using hexane–ether 5:1 mixtures as eluant. The following products, in order of elution, were successively isolated: minor components (5–10%) of type **2** (yellow), **3** (pink) and **4** (violet), and the major product (20–40%) of type **5** (orange) (Scheme I). Thus starting from **1a–d** we were able to isolate and characterize the derivatives $Ru_3(CO)_{10}L_2$ (**2a** and **2d**) and the mixed clusters $FeRu_2(CO)_{10}L_2$ (**3a–d**) possessing two equivalent phosphines and terminal carbonyls only. Structures analogous to that of $Ru_3(CO)_{12}$[13] with the phosphines coordinated only to the ruthenium atoms, can be assigned to these complexes. The derivatives $RuFe_2(CO)_{11}L$ (**4a–d**) show two ν(CO) infrared bands in Nujol corresponding to carbonyl bridges (**4a** 1837, 1805; **4b** 1842, 1802; **4c** 1837, 1795; **4d** 1837, 1800 cm^{-1}). Thus a structure related to that of $Fe_3(CO)_{12}$[14] with two carbonyl bridges between equivalent iron atoms and the phosphine ligand coordinated to ruthenium seems likely. Finally the derivatives $FeRu_2Cl_2(CO)_8L_2$ (**5a–d**) exhibit only terminal ν(CO) bands in the infrared and two equivalent phosphine ligands in the NMR spectra. The only volatile complex of this type, **5a**, shows an ion of *m*/*e* corresponding to $\{FeRu_2Cl_2(CO)_4[P(OMe)_3]_2\}^+$ in the mass spectrum. On the basis of these data, structure **5**, with two equivalent ruthenium atoms, each carrying a tertiary phosphine and bridged by two chloro ligands and a μ-$Fe(CO)_4$ group, was proposed. This type of structure has been confirmed by the single-crystal X-ray diffraction study of **5e**. The reaction of $RuCl_2(L)(C_6H_6)$ (**1**) with $Fe_2(CO)_9$ (Scheme I) thus results in the displacement of the arene and the carbonylation of the vacant coordination sites on the ruthenium atoms with iron–ruthenium bond formation. This allows the synthesis of trimetallic clusters $FeRu_2L_2$, Fe_2RuL, and $FeRu_2Cl_2L_2$ in which the ligands L are solely bound to ruthenium; this assumption is based on the equivalent of phosphorus ligands in complex **3** as shown by NMR and on the X-ray structure of **5e**.

We have also examined the effect of different arenes on the yields of trinuclear products by comparing the dehalogenation of the compounds $RuCl_2(PPh_3)$(arene) containing benzene (**1b**),[7] cymene (**6**),[15] and hexamethylbenzene (**7**).[15] The compound **5b** was obtained in yields of 40%, 34%, and 20%, respectively. Clearly the formation of **5b** decreases with the stability of the arene–ruthenium bond, and therefore the displacement of the arene ligand is an important step for the formation of compounds **5**. The dehalogenation of the derivatives $RuX_2[P(OMe)_3](C_6H_6)$ [**1a** (X = Cl) and **8** (X = I)][7] were also compared: the compounds **2a**, **3a**, and **4a** were formed in similar proportions in the two cases, and 19% of **5a** and 17% of $FeRu_2(\mu\text{-}I)_2(CO)_8[P(OMe)_3]_2$ (**9**) were obtained, respectively. These results suggest that the nature of the halogen does not greatly influence the reaction. While complete dehalogenation occurs when $RuCl_3$ or $[RuCl_2(CO)_3]_2$ are treated in sealed tubes with $Fe(CO)_5$ giving trinuclear carbonyls,[6] the reaction which we have described is interesting in that partial dehalogenation of the derivatives **1** can be accomplished with use of $Fe_2(CO)_9$, producing mixed halo-bridged metal clusters containing the entity $FeRu_2(\mu\text{-}Cl)_2$. This represents a new route to species of the $M_3X_2L_{10}$ type. The complex $Os_3Cl_2(CO)_{10}$[16] has been prepared according to reaction 1, but this method could not, in our hands, be successfully applied to the synthesis of the heteropolymetallic compounds **5** starting from complexes $FeRu_2(CO)_{10}L_2$ (**3**).



$$Os_3(CO)_{12} \xrightarrow{Cl_2} (CO)_4ClOs\text{—}\underset{(CO)_4}{Os}\text{—}OsCl(CO)_4 \xrightarrow[-2CO]{\Delta} Os_3Cl_2(CO)_{10} \quad (1)$$

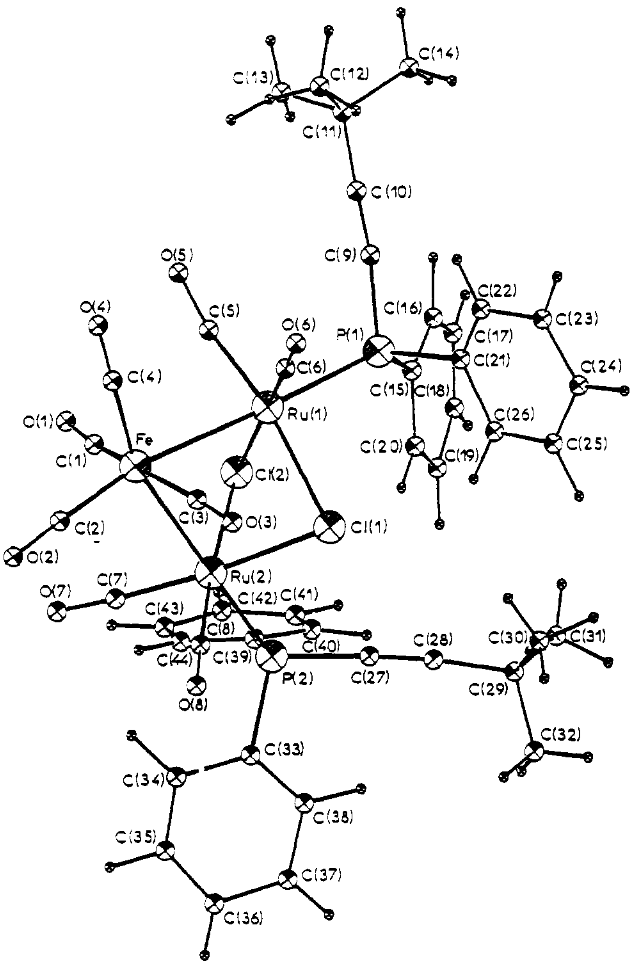


Figure 1. Molecular structure of $FeRu_2(\mu\text{-}Cl)_2(CO)_8(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)_2$ (**5e**).

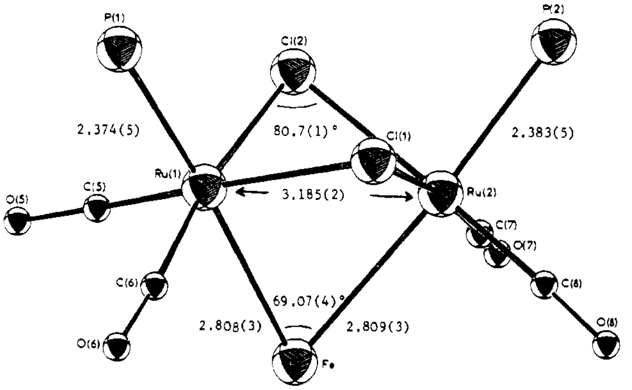


Figure 2. Heavy-atom skeleton of $FeRu_2Cl_2(CO)_8(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)_2$.

The partial dehalogenation method was also applied to the derivative **1e** containing the phosphinoacetylene $Ph_2PC{\equiv}C\text{-}t\text{-}Bu$.[17] In this case only the complex **5e** (30%) was isolated although compounds of type **2–4** were detected in trace quantities by thin-layer chromatography. Under these conditions there was no evidence for insertion into the P–C bond of the phosphinoalkyne, generating phosphido- and acetylido-bridged species, similar to that observed by Carty et al. for $(CO)_4Fe(Ph_2PC{\equiv}CR)$[18] for $M_3(CO)_{11}(Ph_2PC{\equiv}CR)$ (M =

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(13) Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* **1977**, *16*, 2655.

(14) Wei, C. H.; Dahl, L. F. *J. Am. Chem. Soc.* **1966**, *88*, 1821.

(15) Bennett, M. A.; Smith, A. K. *J. Am. Chem. Soc., Dalton Trans.* **1974**, 233.

(16) Deeming, A. J.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc. A* **1970**, 897.

(17) Carty, A. J.; Hota, N. K.; Ng, T. W.; Patel, H. A.; O'Connor, T. J. *Can. J. Chem.* **1971**, 49, 2706.

Table II

Fractional Coordinates (×10^4) for the Nonhydrogen Atoms

atom	x	y	z	atom	x	y	z
Ru(1)	5335 (1)	5868 (1)	7354 (1)	Ru(2)	7741 (1)	6095 (1)	8276 (1)
Fe	7327 (2)	5383 (1)	6959 (2)	Cl(1)	6039 (4)	5662 (2)	8689 (3)
Cl(2)	6361 (4)	6836 (2)	7658 (3)	P(1)	3585 (4)	6225 (2)	7639 (3)
P(2)	8045 (5)	6788 (2)	9317 (3)	C(1)	7500 (15)	6129 (11)	6502 (13)
C(2)	8684 (18)	5128 (10)	6885 (11)	C(3)	7069 (19)	4800 (10)	7631 (14)
C(4)	6636 (19)	4994 (11)	6191 (14)	C(5)	5045 (16)	6065 (9)	6400 (12)
C(6)	4730 (14)	5078 (9)	7194 (13)	C(7)	8975 (13)	6340 (8)	7874 (10)
C(8)	8626 (14)	5491 (9)	8769 (9)	C(9)	2638 (21)	6236 (9)	6829 (13)
C(10)	2034 (17)	6231 (9)	6237 (10)	C(11)	1294 (20)	6218 (10)	5536 (10)
C(12)	1260 (32)	5601 (17)	5197 (19)	C(13)	1734 (24)	6627 (19)	5010 (17)
C(14)	122 (23)	6376 (19)	5638 (17)	C(15)	3465 (15)	7011 (8)	7991 (10)
C(16)	2668 (24)	7415 (10)	7720 (15)	C(17)	2646 (26)	8024 (11)	8002 (15)
C(18)	3443 (26)	8183 (12)	8579 (16)	C(19)	4265 (22)	7789 (13)	8898 (15)
C(20)	4273 (20)	7188 (10)	8604 (14)	C(21)	2860 (14)	5710 (8)	8232 (11)
C(22)	2085 (20)	5323 (11)	7988 (12)	C(23)	1599 (16)	4915 (11)	8437 (15)
C(24)	1941 (18)	4914 (11)	9191 (16)	C(25)	2863 (20)	5268 (11)	9481 (13)
C(26)	3344 (20)	5701 (9)	9020 (11)	C(27)	7074 (18)	6747 (8)	9942 (12)
C(28)	6430 (21)	6685 (9)	10396 (14)	C(29)	5756 (20)	6619 (10)	11002 (11)
C(30)	5140 (26)	6025 (15)	10911 (14)	C(31)	4943 (25)	7137 (15)	11008 (17)
C(32)	6449 (25)	6618 (12)	11739 (13)	C(33)	9336 (20)	6700 (9)	9942 (11)
C(34)	10374 (27)	6562 (14)	9674 (17)	C(35)	11287 (21)	6577 (16)	10165 (18)
C(36)	11342 (27)	6600 (15)	10880 (21)	C(37)	10351 (30)	6680 (17)	11156 (18)
C(38)	9372 (23)	6778 (16)	10690 (15)	C(39)	8044 (17)	7611 (8)	9060 (11)
C(40)	7364 (17)	8029 (9)	9361 (13)	C(41)	7365 (22)	8659 (11)	9141 (17)
C(42)	8056 (20)	8845 (11)	8655 (14)	C(43)	8775 (24)	8452 (12)	8375 (15)
C(44)	8779 (18)	7827 (10)	8611 (13)	O(1)	7526 (12)	6562 (8)	6157 (8)
O(2)	9589 (13)	4914 (8)	6884 (9)	O(3)	6983 (12)	4402 (7)	8028 (10)
O(4)	6160 (14)	4787 (8)	5635 (10)	O(5)	4769 (13)	6185 (7)	5736 (7)
O(6)	4334 (16)	4607 (8)	7041 (11)	O(7)	9696 (13)	6530 (8)	7582 (9)
O(8)	9141 (13)	5085 (7)	9067 (8)				

Anisotropic Thermal Parameters (×10^4) for the Nonhydrogen Atoms[a]

atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ru(1)	58 (1)	14 (0)	24 (1)	−0 (1)	9 (1)	−1 (0)
Ru(2)	55 (1)	17 (0)	23 (0)	−3 (1)	8 (1)	−3 (0)
Fe	71 (3)	22 (1)	25 (1)	5 (1)	13 (1)	−3 (1)
Cl(1)	59 (4)	17 (1)	26 (2)	−2 (2)	16 (2)	2 (1)
Cl(2)	66 (4)	14 (1)	29 (2)	−3 (2)	5 (2)	−1 (1)
P(1)	66 (4)	17 (1)	26 (2)	1 (2)	10 (2)	−1 (1)
P(2)	74 (5)	17 (1)	26 (2)	−2 (2)	10 (2)	−1 (1)
C(1)	37 (15)	35 (7)	49 (10)	7 (9)	14 (10)	3 (7)
C(2)	82 (21)	26 (6)	33 (8)	−10 (9)	−1 (11)	−11 (6)
C(3)	111 (23)	19 (6)	72 (13)	21 (9)	67 (15)	5 (7)
C(4)	94 (22)	28 (7)	45 (9)	22 (7)	13 (11)	6 (7)
C(5)	72 (18)	21 (5)	48 (9)	−20 (8)	14 (11)	−20 (6)
C(6)	25 (14)	25 (6)	61 (11)	−9 (7)	33 (10)	−8 (6)
C(7)	17 (11)	22 (6)	25 (8)	−5 (9)	−15 (11)	−3 (6)
C(8)	38 (14)	25 (5)	22 (8)	−18 (9)	−17 (12)	−5 (5)
C(9)	161 (30)	20 (6)	39 (9)	13 (10)	53 (14)	10 (6)
C(10)	109 (21)	23 (6)	21 (7)	21 (9)	38 (10)	10 (5)
C(11)	143 (25)	26 (6)	17 (7)	1 (10)	32 (11)	−1 (5)
C(12)	257 (52)	61 (13)	83 (18)	53 (21)	−80 (25)	−20 (12)
C(13)	106 (30)	119 (19)	81 (16)	−53 (19)	−76 (17)	69 (15)
C(14)	103 (27)	117 (19)	56 (14)	26 (19)	27 (17)	−33 (14)
C(15)	63 (16)	18 (5)	19 (6)	3 (7)	10 (8)	−1 (4)
C(16)	195 (34)	10 (5)	68 (13)	20 (11)	13 (17)	−3 (7)
C(17)	219 (40)	22 (7)	56 (12)	40 (13)	0 (18)	8 (7)
C(18)	166 (36)	28 (8)	62 (13)	−13 (13)	6 (18)	−17 (8)
C(19)	128 (29)	49 (10)	55 (12)	22 (13)	28 (16)	−10 (9)
C(20)	117 (25)	24 (6)	50 (10)	26 (10)	12 (13)	−13 (7)
C(21)	37 (14)	20 (5)	34 (7)	1 (6)	17 (9)	−1 (5)
C(22)	121 (25)	30 (7)	33 (9)	12 (10)	26 (12)	3 (6)
C(23)	36 (17)	32 (7)	65 (12)	−22 (9)	−1 (12)	5 (8)
C(24)	52 (18)	32 (7)	73 (13)	1 (9)	29 (13)	8 (8)
C(25)	100 (24)	34 (7)	48 (11)	12 (10)	37 (14)	15 (7)
C(26)	135 (25)	21 (6)	28 (8)	4 (9)	29 (12)	2 (5)
C(27)	115 (22)	7 (4)	45 (9)	−8 (7)	25 (12)	−3 (5)
C(28)	156 (28)	12 (5)	56 (11)	10 (9)	50 (15)	15 (6)
C(29)	134 (26)	23 (6)	25 (8)	−4 (10)	18 (12)	2 (5)
C(30)	237 (38)	65 (11)	37 (10)	−73 (18)	43 (16)	−17 (9)
C(31)	177 (33)	59 (12)	78 (15)	67 (17)	71 (19)	35 (11)
C(32)	186 (36)	35 (8)	32 (9)	8 (13)	24 (15)	2 (7)
C(33)	114 (24)	18 (5)	27 (8)	−5 (9)	−18 (11)	−2 (5)
C(34)	177 (37)	49 (11)	58 (14)	34 (16)	−17 (19)	−30 (11)
C(35)	70 (23)	79 (14)	80 (17)	20 (14)	−65 (17)	−48 (13)
C(36)	143 (35)	44 (10)	100 (21)	−6 (15)	−85 (22)	5 (12)

Table II (*Continued*)

atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(37)	156 (38)	71 (15)	63 (16)	−20 (20)	23 (22)	33 (13)
C(38)	122 (28)	76 (14)	45 (12)	−0 (15)	−20 (14)	32 (11)
C(39)	91 (19)	11 (4)	38 (8)	−15 (7)	8 (11)	−6 (5)
C(40)	82 (19)	18 (6)	46 (10)	−1 (8)	−12 (11)	5 (6)
C(41)	112 (26)	25 (7)	86 (16)	41 (11)	27 (17)	6 (8)
C(42)	99 (24)	29 (7)	55 (12)	4 (11)	−7 (13)	−6 (8)
C(43)	174 (34)	32 (8)	61 (13)	−36 (13)	47 (17)	2 (8)
C(44)	89 (21)	27 (6)	56 (11)	−15 (9)	37 (13)	−9 (7)
O(1)	84 (14)	42 (5)	38 (6)	3 (7)	10 (7)	19 (5)
O(2)	96 (16)	48 (6)	53 (8)	20 (8)	13 (9)	−11 (6)
O(3)	74 (13)	21 (4)	71 (8)	7 (6)	14 (9)	2 (5)
O(4)	123 (17)	43 (6)	49 (7)	9 (8)	2 (9)	−20 (6)
O(5)	121 (16)	40 (5)	21 (5)	22 (7)	−1 (7)	8 (4)
O(6)	157 (20)	33 (5)	84 (10)	−43 (9)	53 (12)	−22 (6)
O(7)	93 (15)	51 (6)	43 (6)	−42 (8)	19 (8)	−11 (5)
O(8)	126 (16)	21 (4)	42 (6)	20 (16)	9 (8)	−1 (4)

[a] In the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table III. Selected Interatomic Distances (Å)

Ru(1)–Ru(2)	3.185 (2)	Cl(1)–Cl(2)	3.196 (6)
Ru(1)–Fe	2.808 (3)	Ru(2)–Fe	2.809 (3)
Ru(1)–Cl(1)	2.473 (4)	Ru(2)–Cl(1)	2.468 (5)
Ru(1)–Cl(2)	2.454 (4)	Ru(2)–Cl(2)	2.465 (5)
Ru(1)–P(1)	2.374 (5)	Ru(2)–P(2)	2.383 (5)
Ru(1)–C(5)	1.75 (2)	Ru(2)–C(7)	1.82 (2)
Ru(1)–C(6)	1.87 (2)	Ru(2)–C(8)	1.84 (2)
Fe–C(1)	1.83 (2)	Fe–C(3)	1.80 (2)
Fe–C(2)	1.75 (2)	Fe–C(4)	1.73 (2)
P(1)–C(9)	1.72 (2)	P(2)–C(27)	1.78 (2)
P(1)–C(15)	1.83 (2)	P(2)–C(33)	1.81 (2)
P(1)–C(21)	1.84 (2)	P(2)–C(39)	1.84 (2)
C(1)–O(1)	1.13 (3)	C(5)–O(5)	1.22 (3)
C(2)–O(2)	1.19 (3)	C(6)–O(6)	1.14 (3)
C(3)–O(3)	1.13 (3)	C(7)–O(7)	1.15 (2)
C(4)–O(4)	1.17 (3)	C(8)–O(8)	1.16 (2)
C(9)–C(10)	1.20 (3)	C(27)–C(28)	1.17 (4)
C(10)–C(11)	1.44 (3)	C(28)–C(29)	1.45 (4)
C(11)–C(12)	1.46 (4)	C(29)–C(30)	1.48 (4)
C(11)–C(13)	1.45 (4)	C(29)–C(31)	1.49 (4)
C(11)–C(14)	1.50 (4)	C(29)–C(32)	1.47 (3)

Table IV. Selected Bond Angles (Deg)

Ru(2)–Ru(1)–Fe	55.47 (7)	Ru(1)–Ru(2)–Fe	55.46 (7)
Ru(2)–Ru(1)–Cl(1)	49.81 (9)	Ru(1)–Ru(2)–Cl(1)	49.93 (9)
Ru(2)–Ru(1)–Cl(2)	49.79 (9)	Ru(1)–Ru(2)–Cl(2)	49.51 (9)
Ru(2)–Ru(1)–P(1)	128.1 (1)	Ru(1)–Ru(2)–P(2)	122.4 (1)
Ru(2)–Ru(1)–C(5)	121.2 (4)	Ru(1)–Ru(2)–C(7)	125.4 (3)
Ru(2)–Ru(1)–C(6)	122.2 (4)	Ru(1)–Ru(2)–C(8)	124.9 (3)
Fe–Ru(1)–Cl(1)	89.1 (1)	Fe–Ru(2)–Cl(1)	89.1 (1)
Fe–Ru(1)–Cl(2)	87.1 (1)	Fe–Ru(2)–Cl(2)	86.9 (1)
Fe–Ru(1)–P(1)	176.1 (1)	Fe–Ru(2)–P(2)	174.3 (1)
Fe–Ru(1)–C(5)	84.8 (4)	Fe–Ru(2)–C(7)	83.5 (4)
Fe–Ru(1)–C(6)	87.2 (4)	Fe–Ru(2)–C(8)	92.3 (4)
Cl(1)–Ru(1)–Cl(1)	80.9 (2)	Cl(1)–Ru(2)–Cl(2)	80.8 (2)
Cl(1)–Ru(1)–P(1)	92.8 (2)	Cl(1)–Ru(2)–P(2)	92.8 (2)
Cl(1)–Ru(1)–C(5)	170.9 (5)	Cl(1)–Ru(2)–C(7)	172.5 (4)
Cl(1)–Ru(1)–C(6)	93.4 (5)	Cl(1)–Ru(2)–C(8)	92.3 (4)
Cl(2)–Ru(1)–P(1)	96.6 (2)	Cl(2)–Ru(2)–P(2)	88.2 (2)
Cl(2)–Ru(1)–C(5)	92.2 (5)	Cl(2)–Ru(2)–C(7)	100.1 (4)
Cl(2)–Ru(1)–C(6)	172.0 (5)	Cl(2)–Ru(2)–C(8)	173.0 (4)
P(1)–Ru(1)–C(5)	93.8 (5)	P(2)–Ru(2)–C(7)	94.7 (4)
P(1)–Ru(1)–C(6)	89.3 (5)	P(2)–Ru(2)–C(8)	93.0 (5)
C(5)–Ru(1)–C(6)	92.9 (9)	C(7)–Ru(2)–C(8)	86.7 (8)
Ru(1)–Fe–Ru(2)	69.07 (4)	Ru(1)–Cl(1)–Ru(2)	80.3 (2)
Ru(1)–Fe–C(1)	86.5 (5)	Ru(1)–Cl(2)–Ru(2)	80.7 (1)
Ru(1)–Fe–C(2)	169.0 (4)		
		Ru(1)–P(1)–C(9)	109.5 (6)
Ru(1)–Fe–C(3)	81.9 (5)		
		Ru(1)–P(1)–C(15)	119.5 (4)
Ru(1)–Fe–C(4)	92.6 (5)		
		Ru(1)–P(1)–C(21)	116.0 (5)
Ru(2)–Fe–C(1)	82.9 (5)		
		C(9)–P(1)–C(15)	101.7 (1.0)
Ru(2)–Fe–C(2)	100.1 (4)		
		C(9)–P(1)–C(21)	100.5 (9)
Ru(2)–Fe–C(3)	81.2 (5)		
		C(15)–P(1)–C(21)	107.1 (8)
Ru(2)–Fe–C(4)	161.6 (5)		
C(1)–Fe–C(2)	94 (1)	Ru(2)–P(2)–C(27)	114.6 (5)
C(1)–Fe–C(3)	163 (1)	Ru(2)–P(2)–C(33)	116.7 (6)
C(1)–Fe–C(4)	98 (1)	Ru(2)–P(2)–C(39)	114.6 (5)
C(2)–Fe–C(3)	95 (1)	C(27)–P(2)–C(33)	102.8 (1.0)
C(2)–Fe–C(4)	98 (1)	C(27)–P(2)–C(39)	103.2 (9)
C(3)–Fe–C(4)	95 (1)	C(33)–P(2)–C(39)	103.3 (1.0)

Ru, Os).[19] This point which may have stereochemical implications is discussed later.

Description and Discussion of the Molecular Structure of $\mathbf{FeRu_2(\mu\text{-}Cl)_2(CO)_8(Ph_2PC{\equiv}C\text{-}\mathit{t}\text{-}Bu)_2}$ (5e). A perspective view of the molecular geometry is illustrated in Figure 1 and the heavy-atom skeleton in Figure 2. The structure shows that the heteropolymetallic fragment RuFeRu is a bent chain with two chloro groups bridging the ruthenium atoms. Each phosphorus atom is coordinated to one ruthenium atom in a position trans with respect to each of the Fe–Ru bonds. The other coordination sites on the metals are occupied by terminal carbonyl ligands.

Of special interest is the novel $FeRu_2(\mu\text{-}Cl)_2$ moiety. The Fe–Ru bonds make an angle of 69.07 (4)°, and their lengths are equivalent: Fe–Ru(1) = 2.808 (3) Å and Fe–Ru(2) = 2.809 (3) Å.

The Ru(1)···Ru(2) distance [3.185 (2) Å] is considerably longer than the bonding Ru–Ru contacts in $Ru_3(CO)_{12}$ (average 2.78 Å),[13] $H_2FeRu_3(CO)_{13}$ (average 2.89 Å)[20] or $Ru_3(CO)_5(\eta^5\text{-}C_8H_9)_2$ (2.841 Å)[21] but significantly shorter than the nonbonding distances in the μ-trichloro dimer $Cl(PhEt_2P)_2RuCl_3Ru(PEt_2Ph)_3$ (average 3.367 Å)[22] or in $\{RuCl_2(NO)[(P(O)OEt_2)H]\}_2$ (3.671 Å).[23] The intermediate value for the Ru(1)–Ru(2) distance, between that expected for a strong formal single bond between two ruthenium atoms and that expected in the absence of a covalent interaction, bears a close resemblance to that in the molecule $Ru_3(NO)_2(CO)_{10}$.[24] In the latter that are two strong Ru–Ru bonds

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(18) Carty, A. J.; Mott, G. N.; Taylor, N. J.; Yule, J. E. *J. Am. Chem. Soc.* **1978**, 100, 3051.

(19) Carty, A. J., personal communication.

(20) Gilmore, C. J.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1970**, 245.

(21) Bau, R.; Chou, B. C. K.; Knox, S. A. R.; Riera, V.; Stone, F. G. A. *J. Organomet. Chem.* **1974**, *82*, C43.

(22) Alcock, N. W.; Raspin, K. A. *J. Chem. Soc. A* **1968**, 2108.

(23) Southern, T. G.; Dixneuf, P. H.; Le Marouille, J. Y.; Grandjean, D. *Inorg. Chem.* **1979**, *18*, 2987.

(24) Norton, J. R.; Collman, J. P.; Dolcetti, G.; Robinson, W. T. *Inorg. Chem.* **1972**, *11*, 382.

(average 2.87 Å) and a larger Ru–Ru distance of 3.15 Å. The Ru···Ru distance in **5e** is also to be compared to the PPh_2-bridged ruthenium atom distances of 3.147 (1) and 3.171 (1) Å while the Ru–Ru bond length is 3.098 (1) Å in $FeRu_3(CO)_{13}(\mu\text{-}PPh_2)_2$.[25]

Actually the $FeRu_2(\mu\text{-}Cl)_2$ arrangement in **5e** can be compared directly to the $RuCl_3Ru$ moiety in $Cl_3Sn(CO)_2RuCl_3Ru(CO)_3$[26] by formal displacement of *one* bridging chlorine atom by the $Fe(CO)_4$ group; indeed for this compound the average Ru–Cl distance is 2.44 Å [2.465 (5) Å for **5e**] with a Ru(1)–Cl–Ru(2) angle of 80.7 (4)° [80.7 (2)° for **5e**].

The coordination around the three metal atoms in such that the $FeRu_2Cl_2(CO)_8P_2$ skeleton has approximate C_{2v} symmetry. Both phosphorous atoms lie slightly out of the $FeRu_2$ plane and are unsymmetrically located with respect to the Fe, Cl(1), Cl(2) plane (Table S1). The ruthenium atoms have a distorted octahedral stereochemistry, but the distorsions are similar to that found in $Cl_3Sn(CO)_2RuCl_3Ru(CO)_3$.[26]

The Fe–Ru(1)–P(1) and Fe–Ru(2)–P(2) angles are significantly different: 176.1 (1) and 174.3 (1)°, respectively. The Fe–Ru(1)–C(6) angle [87.2 (4)°] also differs significantly from the Fe–Ru(2)–C(8) angle [92.3 (4)°]. These angular differences may be due to intermolecular steric interaction between $Ph_2PC{\equiv}C$-*t*-Bu ligands of different molecules in the solid state as shown by the short intermolecular distances (Table S2). The bonds within the ligands $Ph_2PC{\equiv}C$-*t*-Bu do not show any particularities; the $PC{\equiv}CC$ chains are roughly linear 174 (2)° and 177 (1)° with a $C{\equiv}C$ bond length of 1.19 (4) Å. The most interesting aspect is the relative positions of the alkyne chains which destroy the C_{2v} symmetry: one is above the $FeRu_2$ plane making an angle of 23° and the other one underneath with an angle of 33°. Moreover the angle between the alkyne chains is 102°, and their relative orientations minimize the interactions between the phenyl groups and the two ligands. These relative positions of the phosphinoalkyne ligands may be responsible for the slight difference between the ruthenium–phosphorus bond lengths [Ru(1)–P(1) = 2.374 (5) Å and Ru(2)–P(2) = 2.383 (5) Å]. Finally, it should be pointed out that there may be a relationship between the reactivity of a coordinated phosphinoalkyne in a polymetallic complex and its relative position with respect to a metal–metal bond. The derivative $Ru_3(CO)_9(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)_3$ for which the phosphinoalkyne ligands lie in a cis position with respect to the Ru–Ru bond[19] undergoes oxidative cleavage of phosphorus–carbon(alkyne) bond affording $Ru_3(CO)_6(\mu\text{-}C_2\text{-}t\text{-}Bu)(\mu\text{-}\eta^2\text{-}C_2\text{-}t\text{-}Bu)(\mu\text{-}PPh_2)_2(Ph_2PC_2\text{-}t\text{-}Bu)$.[27] By contrast for compound **5e** such a behavior was not observed. The inhibition to oxidative cleavage may be due to the presence of chloro bridges but also to the trans position of the phosphinoalkynes with respect to the Fe–Ru bonds.

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Registry No. 1a, 35796-50-0; **1b**, 39732-57-5; **1c**, 39732-59-7; **1d**, 67612-85-5; **1e**, 77187-27-0; **2a**, 78168-08-8; **2d**, 77187-28-1; **3a**, 78168-09-9; **3b**, 77187-30-5; **3c**, 78168-10-2; **3d**, 77187-29-2; **4a**, 78168-11-3; **4b**, 77308-83-9; **4c**, 78168-12-4; **4d**, 77308-84-0; **5a**, 78168-13-5; **5b**, 77187-25-8; **5c**, 78168-14-6; **5d**, 77187-24-7; **5e**, 77187-26-9; **9**, 78168-15-7; $Fe_2(CO)_9$, 15321-51-4.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes, Table S1 (least-squares planes and atomic displacement therefrom), Table S2 (intramolecular interactions), and Figure S1 (unit cell packing) (13 pages). Ordering information is given on any current masthead page.

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[25] Churchill, M. R.; Bueno, C.; Young, D. A., personal communication.
[26] Elder, M.; Hall, D. *J. Chem. Soc. A* **1970**, 245.
[27] Carty, A. J.; Taylor, N. J.; Smith, W. F. *J. Chem. Soc., Chem. Commun.* **1979**, 750.

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Reaction of Lithium Alkyls and Aryls with 1,1′-Diphosphaferrocenes. Synthesis and Structure of a Stable Bis(diene)iron(–I) Species

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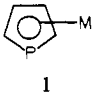
The reaction of 2 equiv of alkyllithium and 3 equiv of alkyl halide with 1,1′-diphosphaferrocene yields a stable green paramagnetic bis(η^4-phospholium)iron halide in which iron bears formally 17 electrons. The stability of these species increases with the bulkiness of the alkyl chains. The product with *tert*-butyl and methyl P substituents was studied by X-ray. The two most striking characteristics of its structure are the absence of a phosphorus–iron bond and the impressive folding of the phospholium nucleus around the Cα–Cα′ axis (≃31°). Crystal data for $FeP_2IC_{22}H_{40}$ are $a = 10.640$ (1) Å, $b = 10.865$ (2) Å, $c = 24.908$ (4) Å, $\alpha = 90.14$ (1)°, $\beta = 95.06$ (1)°, $\gamma = 112.24$ (1)°, $V = 2653$ Å^3, $Z = 4$, $d_{calcd} = 1.37$ g cm^{-3}, and space group $P\bar{1}$. The mechanism of formation of these products probably includes the nucleophilic attack of alkyllithium onto one of the phosphorus atoms of 1,1′-diphosphaferrocene followed by the electrophilic attack of the alkyl halide onto the same phosphorus giving a transient (phospholium)(phospholyl)iron species. When phenyllithium was used, this transient species was spontaneously oxidized and gave a stable (η^4-phospholium)(η^5-1-hydroxy-1-oxophospholato)iron diamagnetic zwitterion, the structure of which was also established by X-ray. The existence of such a compound demonstrates that the phosphole P(O)OH acids are able to chelate a metal between their phosphinate function and their dienic system. Crystal data for $FeP_2O_3C_{19}H_{26}$ are $a = 9.822$ (1) Å, $b = 9.845$ (1) Å, $c = 10.913$ (1) Å, $\alpha = 74.64$ (1)°, $\beta = 67.02$ (1)°, $\gamma = 80.74$ (1)°, $V = 935$ Å^3, $Z = 2$, $d_{calcd} = 1.49$ g cm^{-3}, and space group $P\bar{1}$.

From all the data gathered up to now, it appears that the phosphorus atom of phosphametallocenes **1** has, broadly speaking, lost its classical nucleophilicity and, conversely, acquired some electrophilicity as is the case with phosphorins **2**.[2]



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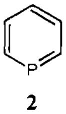

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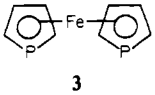

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[2] K. Dimroth, *Top. Curr. Chem.*, **38**, 20 (1973); G. Märkl, *Phosphorus Sulfur*, **3**, 77 (1977); A. J. Ashe III, *Acc. Chem. Res.*, **11**, 153 (1978).

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