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Preliminary communication

A novel mixed platinum–iron cluster compound: Structure of triangulo-tetracarbonyliron–carbonyltris(triphenyl phosphite)diplatinum

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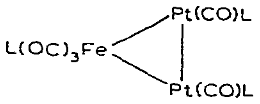
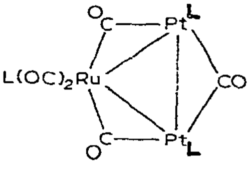
SUMMARY

The complex $FePt_2(CO)_5[P(OPh)_3]_3$ contains a triangular metal-atom cluster and terminally bonded ligands. Coordination about the iron and the platinum atoms is octahedral and square planar, respectively.

The syntheses of substituted trinuclear carbonyls, containing metal-atom clusters in which platinum is bonded to iron, ruthenium, or osmium, have been reported recently[1,2]. Complexes with stoichiometries $M_2Pt(CO)_{10-n}L_n$ (n = 1, 2) and $MPt_2(CO)_5L_3$ (M = Fe, Ru, Os; L = tertiary phosphines, phosphites, or arsines) have been described, and structures suggested on the basis of their IR and NMR spectra. For $Fe_2Pt(CO)_9(PPh_3)$, the proposed structure has been fully confirmed by an X-ray crystallographic study[3].



(I)



(II)

Herein we report the structure of $FePt_2(CO)_5[P(OPh)_3]_3$, obtained from the reaction between $Fe_2(CO)_9$ and $Pt[P(OPh)_3]_4$, which we originally supposed to have structure (I), on the basis of similar ligand transfer reactions found with the ruthenium system. The complex crystallises in orange prisms, m.p. 145–146° (dec.).

Crystal data: $C_{59}H_{45}FeO_{14}P_3Pt_2$, M = 1515.9. Triclinic, a = 22.80(2), b =

12.31(1), $c = 10.55(1)$ Å, $\alpha = 105.2(1)°$, $\beta = 78.0(1)°$, $\gamma = 88.6(1)°$, $U = 2785.7$ Å^3, $D_m = 1.77(2)$, $D_c = 1.81$ g·cm^{-3}. Space group $P1$. The structure has been refined to $R = 0.062$ using 2353 reflections, corrected for absorption ($\mu = 56.9$ cm^{-1}), all having $\sigma(I)/I \leqslant 0.25$ (PAILRED diffractometer, Mo-K_α silicon-monochromatised radiation).

The molecule (see Fig. 1) consists of a closed $FePt_2$ cluster; four terminal CO groups are bonded to iron, with the fifth carbonyl group bonded to Pt(1) *trans* to iron. The three phosphite ligands occupy coordination sites about the platinum atoms resulting in planar geometries.

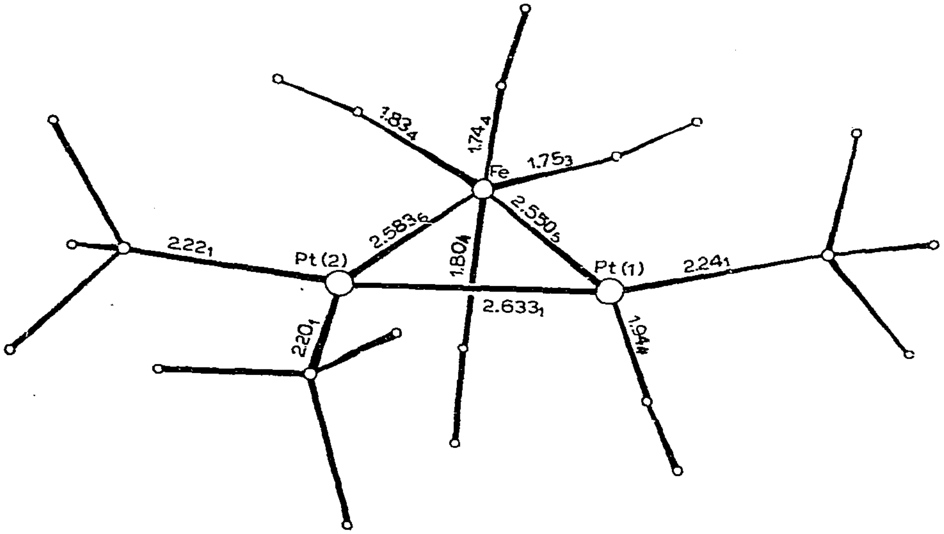


Fig. 1. Molecular structure of $FePt_2(CO)_5\{P(OPh)_3\}_3$.

The two Fe—Pt distances, while not equivalent, differ by only 0.033 Å [compared with 0.079 Å in $Fe_2Pt(CO)_9(PPh_3)$]. The Pt—Pt distance is comparable with that found in $Pt_3(SnCl_3)_2(C_8H_{12})_3$ (2.58 Å)[4], but is shorter than those found in $Pt_4(CO)_5(PPhMe_2)_4$ (2.752, 2.790 Å)[5].

Formally, the complex does not obey the rare gas rule, since each platinum atom attains only a sixteen-electron configuration. However, the metal—metal bonds are shorter than expected for normal electron-pair bonds, and can be considered to have some multiple bond character, so that conventional electron counts are meaningless. Qualitative MO calculations[5] support this structural evidence.

The present result serves to underline the differences found between iron, on the one hand, and ruthenium and osmium, on the other; complexes of stoichiometry $MPt_2(CO)_5L_3$ (M = Ru, Os) contain bridging ν(CO) bands, and probably have structure (II).

ACKNOWLEDGEMENT

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