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# Substituted metal carbonyls

## XV *. Crystal and molecular structures of two isomorphous singly diphosphine-bridged complexes $(OC)_5M(\mu\text{-dppf})M(CO)_5 \cdot CH_2Cl_2$ $(M = Cr, Mo;\ dppf = (Ph_2PC_5H_4)_2Fe)$

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### Abstract

The crystal structures of two dinuclear compounds $(OC)_5M(\mu\text{-dppf})M(CO)_5 \cdot CH_2Cl_2$ (M = Cr, Mo; dppf = $(Ph_2PC_5H_4)_2Fe$), determined by single-crystal X-ray diffraction studies, were found to be isomorphous. (Crystal data: $(OC)_5Cr(\mu\text{-dppf})Cr(CO)_5$, space group *C2/c*, *a* 16.659(3), *b* 15.350(5), *c* 18.877(2) Å, *β* 112.43(2)°, Final *R* 0.046 for 2999 observations. $(OC)_5Mo(\mu\text{-dppf})Mo(CO)_5$, space group *C2/c*, *a* 16.705(4), *b* 15.545(4), *c* 19.091(3) Å, *β* 111.92(2)°, Final *R* 0.037 for 3332 observations). The diphosphine serves as a single bridge between two essentially unperturbed metal carbonyl spheres. The iron was located on a two-fold axis as required crystallographically. The relationship between the phosphinoferrocenyl geometry and the stability of this type of "open" complexes is described together with the solid-state decomposition data from Thermogravimetric (TG) and Differential Scanning Calorimetric (DSC) analyses.

### Introduction

Dinuclear complexes stabilised by diphosphine bridges [1] have attracted considerable research interest largely because of the proposed cooperative effect of the

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* For parts XIII and XIV see refs. 3d and 3e respectively.

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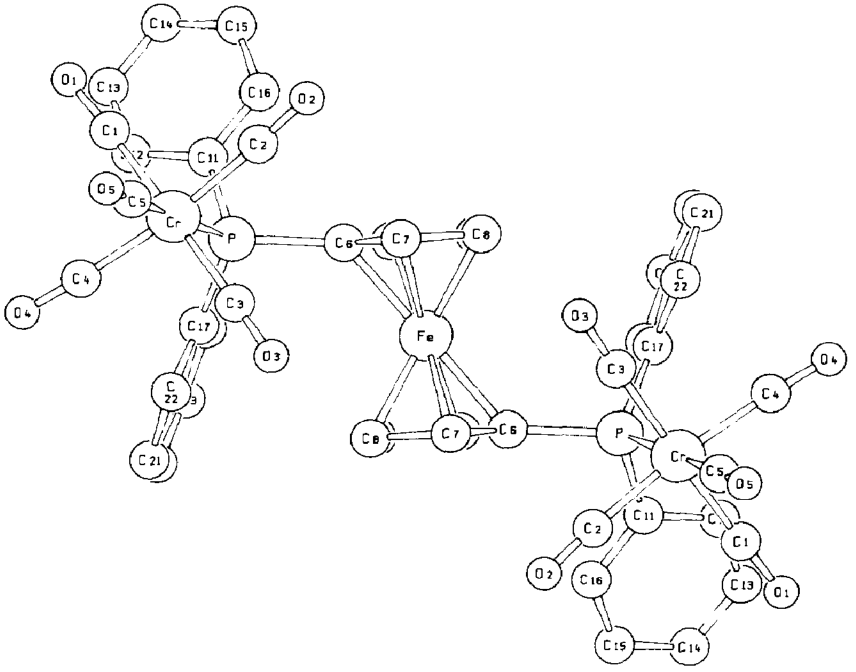

Fig. 1. SCHAKAL plot of $(OC)_5Cr(\mu\text{-dppf})Cr(CO)_5$, **1** (hydrogen atoms are omitted for clarity).

metal centres. Such a vicinity effect by the metals would be further enhanced if the metal–metal bonds and/or other auxiliary bridging ligands like carbonyls are present [2]. In contrast, the open form of the dimers, viz. those which have the highest flexibility in the metal-to-metal bond, while retaining their own electronic integrity are relatively uncommon. We have recently isolated such singly-bridged dinuclear systems in which the metalloligand 1,1′-bis(diphenylphosphino)ferrocene (dppf) was used as the bridging unit [3]. In view of the interest generated by the relationship of the ligand geometry to the chemical and catalytic behaviour of dimetal complexes, we decided to carry out X-ray crystallographic studies on the two Group 6 dimers, $(OC)_5M(\mu\text{-dppf})M(CO)_5$ (M = Cr, **1**, Mo, **2**).

## Results and discussion

The two complexes were found to be isomorphous and hence their analyses will be described jointly. Both complexes are solvated by a disordered $CH_2Cl_2$ molecule. Single crystals of the dimeric tungsten analogue were also grown , whose preliminary X-ray data suggested the complex to be isomorphous to **1** and **2**; full intensity data collection is hence unnecessary. The following descriptions are also judged to be applicable to the W dimer.

Both structures consist of a dppf unit bridging between two pentacarbonyl metal moieties through the phosphine groups (Figs. 1 and 2). The ferrocenyl iron atom was located on a two-fold axis as required crystallographically. The octahedral geometry about the two metal spheres is essentially undisturbed. No unusual features are shown by the carbonyl groups, except the slight sweeping back of a set of "equatorial" carbonyls (C(2)–Cr–C(4) = 173.56(24)° and C(2)–Mo–C(4) =

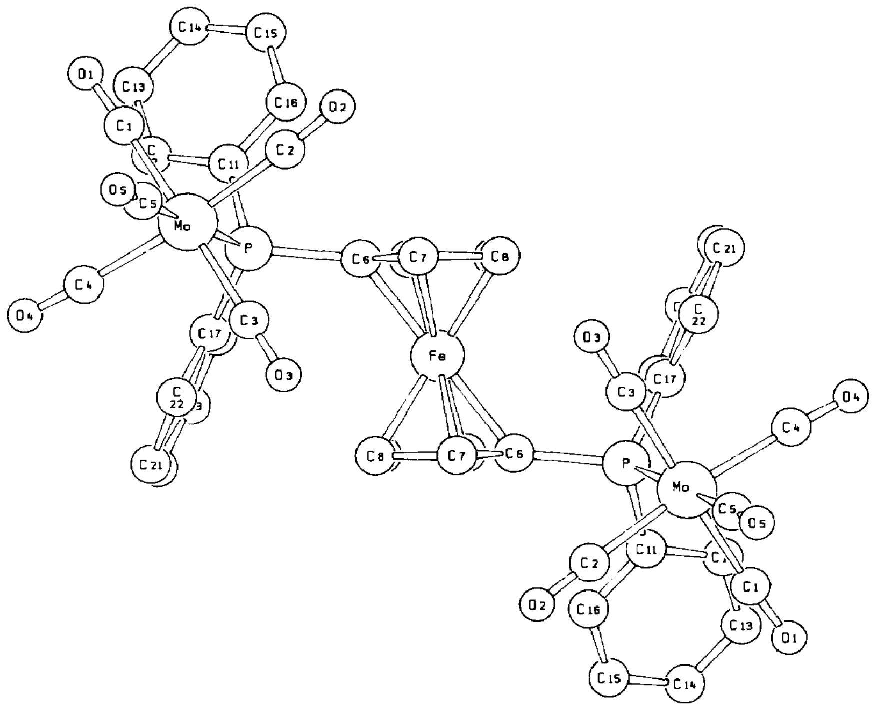

Fig. 2. SCHAKAL plot of $(OC)_5Mo(\mu\text{-dppf})Mo(CO)_5$, 2 (hydrogen atoms are omitted for clarity).

174.43(23)°) probably because of the steric influence by the phenyl rings. The lower *trans* influence of the phosphine is reflected in the slight shortening of the M–CO bonds in the *trans* carbonyl.

A close examination of the ferrocenyl group is essential before one can compare the constraint in the title complexes with the chelate. The near linear P ··· Fe ··· P′ angle of 174.70(5)° for **1** and 174.78(4)° for **2** creates a large "pocket" between the metal spheres. Such a large bite of the bridging ligand is ensured mainly by a large torsional twist of C(6) ··· Centroid ··· Centroid′ ··· C(6)′ (171.6(3)° for **1** and 173.2(3)° for **2**), which secures a minimum steric hindrance and evenly distributes the metals in the crystalline state (Cr ··· Cr and Mo ··· Mo intermolecular distances of 5.213(1) and 5.629(1) Å; Fe ··· Cr and Fe ··· Mo intramolecular distances of 5.115(1) and 5.213(1) Å, respectively) and to a lesser extent, by a staggered conformation of the parallel cyclopentadienyl (Cp) rings with a slight rotation of 7.8° (28.2° from the eclipsed form) for **1** and 7.3° (28.7° from the eclipsed) for **2**. A similar *anti* (or *trans*) conformation is also apparent in a recently reported structure of $Cl(OC)_4Mn(\mu\text{-dppf})Mn(CO)_4Cl$ [4]. Further flexibility of the bridge unit is facilitated by a mild displacement of the P atoms from the Cp rings away from the ferrocenyl iron atom by 0.189(9) Å for **1** and 0.198(9) Å for **2**. The non-rigidity of the rings allows a maximum separation of the P atoms (P ··· P′ 7.073(3) for **1** and 7.062(3) Å for **2**) and widening of the P ··· Fe ··· P′ angle. These features are in sharp contrast to those found in the dinuclear complexes bridged by dppm where the bite is understandably smaller owing to the narrower P–C–P′ angle (100–120°) and shorter P ··· P′ separation (2.9–3.1 Å) [5]. The versatility of the ligation mode of dppm is largely due to the variability of the P–C–P′ angle.

Recent findings in our laboratories [3,6] showed that dppf is sufficiently adapted to ligate in the bridging, chelating and unidentate fashion. In contrast, such flexibility of the dppf is attributed to the ability of the Cp rings to twist and tilt, and the P atoms to deviate from planarity with the rings.

A comparison of the present data with those of $Mo(CO)_4(dppf)$ [7] immediately revealed the marginally higher distortion of the ferrocenyl group in the chelate. Though the substituent-induced distortions on the phosphinated carbons are comparable in both cases, there is no significant variation in the Fe–C(ring) lengths in **1** (2.036–2.060 Å) and **2** (2.042–2.061 Å) with the shortest Fe–C bonds belonging to C(10) whereas the Mo chelate shows the shortest distances for the substituted C atoms. The cyclopentadienyl rings are planar (within experimental error—maximum displacement 0.005 Å) and parallel (angles between the normals to the plane are 1.3° for both complexes) thus comparable to the rings in the chelate (angles between the plane normals = 2.2°). The Cp rings in dppf has shown great adaptability with respect to ring tilting, e.g. 6.2° in $Pd(dppf)Cl_2$ [7] and 1.8° in $Fe(CO)_3(dppf)$ [6a]. The chelate conformation in $Mo(CO)_4(dppf)$ also forces the P atoms to tilt inwards rather than outwards as observed in the present cases. The non-rigidity of the P atoms is believed to play a fundamental role in the stabilisation of complexes of different local geometries. It also allows the dppf to stabilise metal ions of different sizes. All these observations, together with the shorter though not statistically significant Mo–P length in **2** (2.532(1) Å) than that in the tetracarbonyl chelate (2.560(16) Å), are consistent with our previous NMR data [3b] which suggested that the metalloligand is less strained in the bridging state. Like the title dimers, dppf in its free state [8] adopts an *anti* conformation with the two Cp rings parallel and staggered to result in centrosymmetry with the iron atom at the inversion centre. Such resemblances lend further support to the fact that dppf is more a bridging than a chelating ligand. As yet we have no evidence that such structural differences can be translated in terms of the relative stability of the two systems. A brief examination of these systems has in fact revealed a higher kinetic and thermodynamic stability of the chelates. The kinetic preference of the chelates is exemplified in a typical room temperature preparation under the stoichiometric ratio for $M(CO)_6$ : dppf : TMNO of 1 : 0.4 : 0.8 for which the yields of the chelates for all the Group 6 metals are inevitably higher. In toluene under reflux, the bridging complexes rearrange to give the chelates as the major isolable products, except that for W only partial conversion is observed [9]. The lower thermal stability of the title complexes is also reflected in their solid-state. Thermogravimetric (TG) and Differential Thermalgravimetric (DTG) analyses suggested that, under a dynamic flow of $N_2$, degradation of the dimers commences at least 30 °C lower than that of the chelates and that the dimers indeed give rise to the chelates at the initial decompositional step. The latter point is eminently clear in the Differential Scanning Calorimetric (DSC) plots of **1** and **2** where the enthalpic changes of the dimer can be interpreted in terms of the melting of the complex, followed immediately by the decarbonylation and chelation, and then the melting of the chelate and subsequently its degradation. These features are best illustrated in the TG (Fig. 3) and DSC (Fig. 4) thermograms of **2** and its associated chelate. These solution and solid-state data show that the adaptability of dppf as a ligand in different local geometrical environments is unrivalled among the common diphosphines. It may be this distinctive feature of dppf which empowers its complexes to enjoy such high

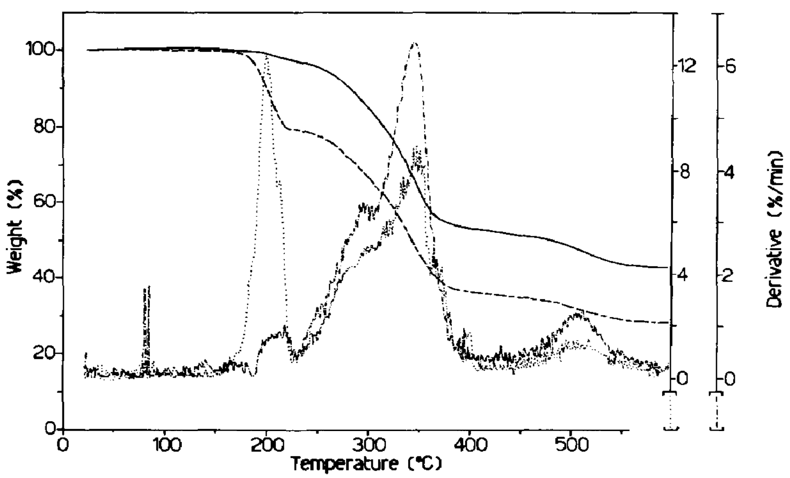

Fig. 3. TG and DTG profiles of **2** (- — — —, · · · · · ·, respectively) and Mo(CO)$_4$(dppf) (———, ·—·—·, respectively).

catalytic activity in numerous cross-coupling, hydroformylation and hydrogenation reactions [10].

## Conclusion

Of the common difunctional phosphines, dppm has the richest chemistry [11], dppe is abundantly found in chelates [12] while the higher membered analogues are believed to favour the bridging form [13]. Many of the isolated dppf complexes are chelates [14]. However, as the present structural studies show, the bridging form of the ligand has the advantage of linking two essentially unperturbed metal spheres with little bearing on the strain of the bridge. This naturally raises some fundamental questions on the comparative chemistry of these open singly-bridged dimers and the well-established A-frame molecules [15]. The presence of an "extra" metal centre on the bridge adds more essence to this piece of research.

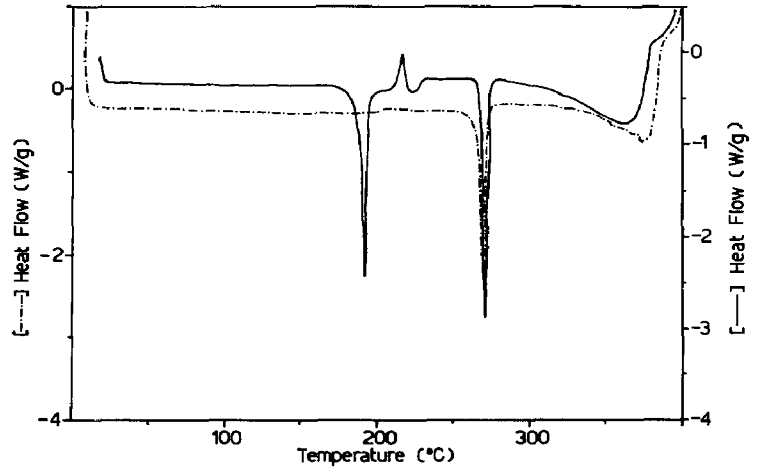

Fig. 4. DSC profiles of **2** (———) and Mo(CO)$_4$(dppf) (·—·—·).

## Experimental

### *General procedures and syntheses*

All syntheses and characterisations follow those routinely carried out in this laboratory [3]. Preparations of $M_2(CO)_{10}(\mu\text{-dppf})$ M = Cr, Mo, W) have been described previously [3b]. The TG and DSC experiments were conducted by use of a Du Pont 9900 thermal analyser under similar conditions as reported [16].

Table 1

Crystallographic data and refinement details for $(dppf)[M(CO)_5]_2$ (M = Cr, **1** and Mo, **2**)

| | M = Cr | M = Mo |
|---|---|---|
| Space group | *C*2/*c* | *C*2/*c* |
| *a*, Å | 16.659(3) | 16.705(4) |
| *b*, Å | 15.350(5) | 15.545(4) |
| *c*, Å | 18.877(2) | 19.091(3) |
| $\beta$, deg. | 112.428(12) | 111.920(17) |
| *V*, $Å^3$ | 4461.8(16) | 4599.2(17) |
| Empirical formula | $C_{45}H_{30}Cl_2Cr_2FeO_{10}P_2$ | $C_{45}H_{30}Cl_2FeMo_2O_{10}P_2$ |
| Crystal dimensions, mm | 0.48 × 0.28 × 0.32 | 0.46 × 0.40 × 0.33 |
| FW | 1023.45 | 1111.33 |
| *Z* | 4 | 4 |
| *F*(000) | 2071.74 | 2215.44 |
| $D_{\text{calc}}$, g $cm^{-3}$ | 1.524 | 1.605 |
| $\mu$, $mm^{-1}$ | 1.03 | 1.07 |
| $\lambda$, Å | 0.7093 | 0.7093 |
| $2\theta$(max) | 49.8 | 49.8 |
| Diffractometer | Nonius CAD4 | Nonius CAD4 |
| Scan mode | $\theta/2\theta$ | $\theta/2\theta$ |
| Data ranges | $-19 < h < 18$,<br>$0 < k < 18$,<br>$0 < l < 22$ | $-19 < h < 18$,<br>$0 < k < 18$,<br>$0 < l < 22$ |
| Unique reflections | 3930 | 4039 |
| Observations $I > 2\sigma(I)$ | 2999 | 3332 |
| Absorption corrections | Yes | Yes |
| Transmission factors | 0.973–1.000 | 0.957–1.000 |
| Total atoms | 47 | 47 |
| Parameters | 347 | 346 |
| Weights | counting-statistics | counting-statistics |
| Weight modifier | – | 0.01 |
| $R_F$ | 0.046 | 0.037 |
| $R_w$ | 0.056 | 0.046 |
| Goodness of fit | 4.87 | 2.49 |
| Max shift/$\sigma$ | 0.522 | 0.929 [a] |
| Peaks in *D*-map, e/$Å^3$ | | |
| high | 1.040 [b] | 0.730 |
| low | −0.880 | −0.610 |
| secondary extinction coefficient | 9.4(9) | – |

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[a] If parameters other than those for the solvate molecule are considered, the maximum shift/sigma ratio was only 0.05. [b] The highest peak 1.040 e/$Å^3$ was located in the neighbourhood of Cl1, a chlorine atom of the solvate molecule, at 2.42 Å.

Table 2

Final fractional coordinates for (dppf)$[Cr(CO)_5]_2$

| Atom | $x$ | $y$ | $z$ | $B$(iso), Å$^2$ [a] |
|---|---|---|---|---|
| Cr | 0.28993(5) | 0.85516(5) | 0.89617(5) | 3.33(4) |
| Fe | 0.00000 | 0.00640(7) | 0.75000 | 2.76(5) |
| P | 0.22596(8) | 0.99574(9) | 0.85961(7) | 2.62(6) |
| O1 | 0.4684(3) | 0.9200(3) | 0.9146(3) | 7.1(3) |
| O2 | 0.2585(3) | 0.8078(3) | 0.7317(2) | 6.4(3) |
| O3 | 0.1140(3) | 0.7884(3) | 0.8839(2) | 5.5(2) |
| O4 | 0.3502(3) | 0.8997(3) | 1.0643(2) | 6.7(3) |
| O5 | 0.3642(3) | 0.6764(3) | 0.9367(3) | 7.9(3) |
| C1 | 0.4004(4) | 0.8968(4) | 0.9060(3) | 4.4(3) |
| C2 | 0.2684(4) | 0.8276(4) | 0.7925(3) | 4.2(3) |
| C3 | 0.1802(4) | 0.8135(3) | 0.8881(3) | 3.9(3) |
| C4 | 0.3246(4) | 0.8825(4) | 1.0008(3) | 4.2(3) |
| C5 | 0.3366(4) | 0.7451(4) | 0.9216(3) | 5.1(4) |
| C6 | 0.1307(3) | 0.0011(3) | 0.7713(2) | 2.7(2) |
| C7 | 0.0862(3) | −0.0683(4) | 0.7232(3) | 3.1(3) |
| C8 | 0.0231(3) | −0.0342(4) | 0.6563(3) | 3.6(3) |
| C9 | 0.0269(3) | 0.0566(4) | 0.6611(3) | 3.8(3) |
| C10 | 0.0925(3) | 0.0795(4) | 0.7320(3) | 3.3(3) |
| C11 | 0.3017(3) | 0.0688(3) | 0.8398(3) | 2.7(2) |
| C12 | 0.3673(3) | 0.1094(4) | 0.8996(3) | 3.6(3) |
| C13 | 0.4305(4) | 0.1564(4) | 0.8863(4) | 4.5(3) |
| C14 | 0.4294(4) | 0.1633(4) | 0.8137(4) | 4.8(4) |
| C15 | 0.3657(4) | 0.1222(4) | 0.7540(4) | 4.6(3) |
| C16 | 0.3020(3) | 0.0751(4) | 0.7668(3) | 3.5(3) |
| C17 | 0.1950(3) | 0.0577(3) | 0.9282(3) | 3.0(2) |
| C18 | 0.1863(3) | 0.1474(4) | 0.9239(3) | 3.9(3) |
| C19 | 0.1571(4) | 0.1910(5) | 0.9741(5) | 5.4(4) |
| C20 | 0.1365(4) | 0.1474(6) | 1.0274(4) | 5.9(4) |
| C21 | 0.1455(4) | 0.0594(6) | 1.0320(4) | 5.3(4) |
| C22 | 0.1734(4) | 0.0143(4) | 0.9823(3) | 3.7(3) |
| C23 | 0.4691(11) | 0.0785(10) | 0.2298(8) | 8.5(12) |
| Cl1 | 0.5000 | 0.1875(4) | 0.2500 | 21.9(6) |
| Cl2 | 0.3811(4) | 0.0966(4) | 0.1603(5) | 15.5(6) |
| H7 | 0.096(3) | −0.123(2) | 0.737(2) | 1.6(9) |
| H8 | −0.017(3) | −0.068(3) | 0.618(2) | 3.3(11) |
| H9 | −0.009(3) | 0.097(3) | 0.627(3) | 3.7(12) |
| H10 | 0.107(3) | 0.134(2) | 0.749(2) | 2.1(10) |
| H12 | 0.369(3) | 0.102(3) | 0.949(2) | 2.5(10) |
| H13 | 0.476(3) | 0.183(3) | 0.927(3) | 3.9(12) |
| H14 | 0.474(3) | 0.194(3) | 0.807(3) | 4.6(13) |
| H15 | 0.362(3) | 0.129(3) | 0.706(3) | 3.9(13) |
| H16 | 0.256(3) | 0.049(3) | 0.724(2) | 3.9(12) |
| H18 | 0.197(3) | 0.182(3) | 0.885(2) | 2.9(11) |
| H19 | 0.152(3) | 0.246(3) | 0.963(3) | 4.6(16) |
| H20 | 0.118(4) | 0.175(4) | 1.069(3) | 8.1(18) |
| H21 | 0.133(3) | 0.032(3) | 1.064(3) | 5.1(16) |
| H22 | 0.178(3) | −0.040(3) | 0.985(2) | 2.6(12) |

[a] Mean of the principal axes of the thermal ellipsoid.

Table 3

Selected bond distances (Å) and angles (deg) for (dppf)[Cr(CO)$_5$]$_2$

| | | | |
|---|---|---|---|
| Fe–C(6) | 2.060(4) | Cr–C(5) | 1.846(6) |
| Fe–C(7) | 2.046(5) | P–C(6) | 1.812(4) |
| Fe–C(8) | 2.046(5) | P–C(11) | 1.829(5) |
| Fe–C(9) | 2.046(6) | P–C(17) | 1.833(5) |
| Fe–C(10) | 2.036(5) | O(1)–C(1) | 1.138(7) |
| Cr–P | 2.389(2) | O(2)–C(2) | 1.138(7) |
| Cr–C(1) | 1.890(6) | O(3)–C(3) | 1.142(7) |
| Cr–C(2) | 1.898(6) | O(4)–C(4) | 1.139(7) |
| Cr–C(3) | 1.887(6) | O(5)–C(5) | 1.142(7) |
| Cr–C(4) | 1.881(6) | | |
| P–Cr–C(1) | 91.9(2) | C(3)–Cr–C(5) | 90.6(3) |
| P–Cr–C(2) | 90.9(2) | C(4)–Cr–C(5) | 90.1(3) |
| P–Cr–C(3) | 88.3(2) | Cr–C(1)–O(1) | 177.2(5) |
| P–Cr–C(4) | 91.5(2) | Cr–C(2)–O(2) | 176.6(5) |
| P–Cr–C(5) | 178.1(2) | Cr–C(3)–O(3) | 179.5(5) |
| C(1)–Cr–C(2) | 88.3(2) | Cr–C(4)–O(4) | 176.2(5) |
| C(1)–Cr–C(3) | 179.1(2) | Cr–C(5)–O(5) | 178.9(6) |
| C(1)–Cr–C(4) | 85.7(2) | C(7)–C(6)–C(10) | 106.3(4) |
| C(1)–Cr–C(5) | 89.2(3) | C(6)–C(7)–C(8) | 109.1(5) |
| C(2)–Cr–C(3) | 92.6(2) | C(7)–C(8)–C(9) | 108.3(5) |
| C(2)–Cr–C(4) | 173.6(2) | C(8)–C(9)–C(10) | 108.0(5) |
| C(2)–Cr–C(5) | 87.6(3) | C(6)–C(10)–C(9) | 108.3(5) |
| C(3)–Cr–C(4) | 93.4(2) | | |

*Crystallographic analyses*

Large orange single crystals of complexes **1** and **2** were grown from a solution of hexane/CH$_2$Cl$_2$ mixture. Single crystals suitable for X-ray diffraction were mounted on top of a glass fiber with epoxy glue for preliminary characterization and intensity data collection. The crystallographic data and refinement details of **1** and **2** are listed in Table 1. The structures were solved by the three heavy atom, Patterson methods (M, Fe, P, where M = Cr for **1**, and M = Mo for **2**) and were found to be isomorphous. The ferrocenyl Fe atom was located along a two-fold axis as required crystallographically. The crystal structures were found to have disordered CH$_2$Cl$_2$ molecules around a crystallographic two-fold axis. All hydrogen atoms were found at anisotropic convergence and included as isotropic ellipsoids in the final cycles of least-squares refinement. The non-hydrogen atoms were varied anisotropically. The atomic scattering curves of Mo, Fe, Cr, Cl, P, O, C, and H were taken from *International Tables for X-Ray Crystallography*, Volume IV. Computations were carried out on a MicroVAX 3600 with NRCC package [17]. The respective structures of **1** and **2** are shown in Figs. 1 and 2. Final atomic fractional coordinates and selected bond distances and angles for **1** are listed in Tables 2 and 3 and those for **2** in Tables 4 and 5, respectively.

*Supplementary material.* Lists of thermal parameters and final structure factors for (dppf)[M(CO)$_5$]$_2$ (M = Cr, **1** and Mo, **2**) are available from the authors.

Table 4

Final fractional coordinates for $(dppf)[Mo(CO)_5]_2$

| Atom | x | y | z | B(iso), Å$^2$ |
|---|---|---|---|---|
| Mo | 0.28982(3) | −0.14631(3) | 0.89654(2) | 3.27(2) |
| Fe | 0.00000 | 0.01157(7) | 0.7500 | 2.82(5) |
| P | 0.22370(7) | 0.00121(8) | 0.85823(6) | 2.64(5) |
| O1 | 0.4757(3) | −0.0767(4) | 0.9173(3) | 7.9(3) |
| O2 | 0.2575(3) | −0.1960(4) | 0.7268(3) | 7.2(3) |
| O3 | 0.1049(3) | −0.2123(3) | 0.8831(3) | 6.2(3) |
| O4 | 0.3484(3) | −0.0995(4) | 1.0693(2) | 7.0(3) |
| O5 | 0.3672(4) | −0.3313(3) | 0.9396(3) | 8.5(4) |
| C1 | 0.4086(4) | −0.1007(4) | 0.9079(3) | 4.6(3) |
| C2 | 0.2671(4) | −0.1768(4) | 0.7867(4) | 4.5(3) |
| C3 | 0.1717(4) | −0.1894(4) | 0.8884(3) | 4.2(3) |
| C4 | 0.3247(4) | −0.1164(4) | 1.0073(3) | 4.5(3) |
| C5 | 0.3400(5) | −0.2632(4) | 0.9243(4) | 5.4(3) |
| C6 | 0.1297(3) | 0.0078(3) | 0.7714(2) | 2.9(2) |
| C7 | 0.0871(3) | −0.0626(4) | 0.7236(3) | 3.3(2) |
| C8 | −0.0242(3) | −0.0283(4) | 0.8428(3) | 3.8(3) |
| C9 | −0.0281(3) | 0.0611(4) | 0.8375(3) | 4.0(3) |
| C10 | 0.0923(3) | 0.0843(4) | 0.7320(3) | 3.5(2) |
| C11 | 0.3004(3) | 0.0712(3) | 0.8387(3) | 2.8(2) |
| C12 | 0.3659(3) | 0.1110(4) | 0.8977(3) | 3.7(3) |
| C13 | 0.4297(4) | 0.1566(4) | 0.8841(4) | 4.6(3) |
| C14 | 0.4291(4) | 0.1634(4) | 0.8130(4) | 5.1(3) |
| C15 | 0.3659(4) | 0.1242(4) | 0.7540(4) | 5.0(3) |
| C16 | 0.3006(3) | 0.0777(4) | 0.7665(3) | 3.7(3) |
| C17 | 0.1926(3) | 0.0632(3) | 0.9255(3) | 3.3(2) |
| C18 | 0.1844(4) | 0.1518(4) | 0.9219(4) | 4.4(3) |
| C19 | 0.1552(4) | 0.1951(5) | 0.9714(5) | 5.8(4) |
| C20 | 0.1353(5) | 0.1513(6) | 1.0247(4) | 6.5(4) |
| C21 | 0.1430(4) | 0.0633(6) | 1.0288(4) | 5.9(4) |
| C22 | 0.1715(3) | 0.0195(4) | 0.9794(3) | 3.9(3) |
| C23 | 0.4630(14) | 0.0777(16) | 0.2280(9) | 11.0(15) |
| Cl1 | 0.5000 | 0.1857(5) | 0.2500 | 22.6(8) |
| Cl2 | 0.3776(7) | 0.0930(5) | 0.1601(7) | 17.2(8) |
| H7 | 0.102(3) | −0.123(3) | 0.740(3) | 3.5(11) |
| H8 | 0.017(3) | −0.066(3) | 0.880(3) | 4.4(12) |
| H9 | 0.005(3) | 0.097(3) | 0.869(3) | 3.8(12) |
| H10 | 0.106(3) | 0.138(3) | 0.752(3) | 3.7(12) |
| H12 | 0.369(3) | 0.103(3) | 0.946(3) | 2.8(10) |
| H13 | 0.475(4) | 0.187(4) | 0.923(3) | 6.5(16) |
| H14 | 0.473(4) | 0.200(4) | 0.805(3) | 6.9(16) |
| H15 | 0.360(4) | 0.135(4) | 0.705(4) | 5.8(16) |
| H16 | 0.259(3) | 0.046(3) | 0.725(3) | 3.4(11) |
| H18 | 0.200(3) | 0.179(3) | 0.884(3) | 3.8(12) |
| H19 | 0.150(4) | 0.251(4) | 0.959(3) | 4.4(14) |
| H20 | 0.114(4) | 0.185(4) | 1.059(4) | 7.1(17) |
| H21 | 0.130(4) | 0.033(5) | 1.063(4) | 6.8(19) |
| H22 | 0.176(3) | −0.043(4) | 0.983(3) | 4.5(13) |

Table 5

Selected bond distances (Å) and angles (deg) for (dppf)$[Mo(CO)_5]_2$

| | | | |
|---|---|---|---|
| Mo–P | 2.532(1) | Fe–C(9) | 2.046(5) |
| Mo–C(1) | 2.040(6) | Fe–C(10) | 2.042(5) |
| Mo–C(2) | 2.044(6) | P–C(6) | 1.811(5) |
| Mo–C(3) | 2.034(6) | P–C(11) | 1.823(5) |
| Mo–C(4) | 2.027(6) | P–C(17) | 1.830(5) |
| Mo–C(5) | 1.989(7) | O(1)–C(1) | 1.131(8) |
| Fe–C(6) | 2.050(4) | O(2)–C(2) | 1.132(8) |
| Fe–C(7) | 2.061(5) | O(3)–C(3) | 1.139(8) |
| Fe–C(8) | 2.055(5) | O(4)–C(4) | 1.128(8) |
| | | O(5)–C(5) | 1.146(8) |
| | | | |
| P–Mo–C(1) | 91.0(2) | C(3)–Mo–C(4) | 92.7(2) |
| P–Mo–C(2) | 91.2(2) | C(3)–Mo–C(5) | 91.1(3) |
| P–Mo–C(3) | 88.3(2) | C(4)–Mo–C(5) | 90.2(3) |
| P–Mo–C(4) | 91.1(2) | Mo–C(1)–O(1) | 177.1(5) |
| P–Mo–C(5) | 178.7(2) | Mo–C(2)–O(2) | 177.2(5) |
| C(1)–Mo–C(2) | 89.4(2) | Mo–C(3)–O(3) | 178.8(5) |
| C(1)–Mo–C(3) | 178.0(2) | Mo–C(4)–O(4) | 176.4(5) |
| C(1)–Mo–C(4) | 85.4(2) | Mo–C(5)–O(5) | 178.5(7) |
| C(1)–Mo–C(5) | 89.6(3) | C(7)–C(6)–C(10) | 106.7(4) |
| C(2)–Mo–C(3) | 92.4(2) | C(6)–C(7)–C(8) | 108.0(5) |
| C(2)–Mo–C(4) | 174.4(2) | C(7)–C(8)–C(9) | 108.2(5) |
| C(2)–Mo–C(5) | 87.7(3) | C(8)–C(9)–C(10) | 108.8(5) |
| | | C(6)–C(10)–C(9) | 108.3(5) |

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