A Novel Binuclear Rhodium Complex Containing Bridging Methylene and Acetylene Ligands not Accompanied by a Metal–Metal Bond

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Since the first synthesis of a complex containing a bridging methylene moiety [1, 2] there has been increasing interest in these compounds for their applications both in synthetic organometallic chemistry and as potential model systems for metallic surface catalysts; bridging methylene units are believed to play an important role in olefin metathesis [3] and Fischer–Tropsch-type reactions [4, 5]. However, until recently, only metal–metal bonded methylene-bridged species were known [2]. We were therefore interested in extending the range of methylene-bridged complexes to include those not accompanied by a metal–metal bond on the assumption that the geometry of and the charge distribution within the $M-CH_2-M$ fragment could significantly influence the role of the methylene bridge in a reaction. Recently two reports of such species have appeared; $[Pt_2Cl_2(\mu\text{-}CH_2)(DPM)_2]$ was prepared by CH_2 insertion into the Pt–Pt single bond of the precursor [6] and $[Pd_2X_2(\mu\text{-}CH_2)(DPM)_2]$ (X = Cl, Br, I) were prepared by oxidative addition of CH_2X_2 to a Pd(0) species [7]. Although the formulations of these Pd and Pt species seem clear, structural confirmation is still lacking and the geometries of the $M-CH_2-M$ fragments are not known.

As part of our continuing interest in metal–metal single-bond reactivity [8, 9], we investigated the possible insertions of methylene fragments into Rh–Rh single bonds and here report our preliminary results on the synthesis, spectral characterization and structure of $[Rh_2Cl_2(\mu\text{-}CH_2)(\mu\text{-}HFB)(DPM)_2]$ (*1*) (HFB = $CF_3C_2CF_3$, DPM = $Ph_2PCH_2PPh_2$), the first bridging methylene complex without an accompanying metal–metal bond to be characterized by X-ray crystallography.

Compound *1* was prepared by the reaction of $[Rh_2Cl_2(\mu\text{-}HFB)(DPM)_2]$ (*2*) [10] (85 mg in 15 ml of CH_2Cl_2) with a diethyl ether solution of diazomethane (2.4 g in 5 ml Et_2O) under a dinitrogen atmosphere at $-78\ ^\circ C$. In addition to the phenyl resonances, the ^1H NMR spectrum of *1* shows three
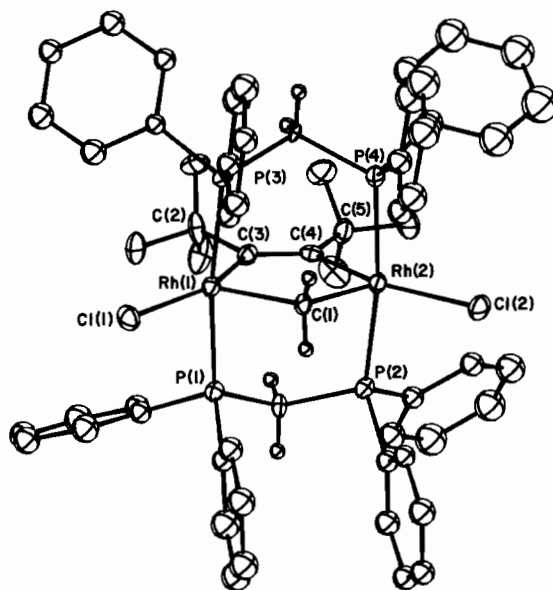

Fig. 1. A perspective view of $[Rh_2Cl_2(\mu\text{-}CH_2)(\mu\text{-}HFB)(DPM)_2]$ showing 20% thermal ellipsoids. The methylene hydrogen atoms are drawn in their idealized locations with artificially small thermal parameters.

resonances, each consistent with two protons, corresponding to the DPM methylene groups ($\delta = 3.15$ and 4.02 ppm) and the dimetallated methylene group at $\delta = 6.07$ ppm. The two methylene protons of each DMP ligand are inequivalent and therefore appear as an AB quartet in which each peak is further split into a quintet owing to virtual coupling with the four phosphorus atoms and the resonance due to the dimetallated methylene protons appears as a quintet due to coupling with the four equivalent ^{31}P nuclei ($^3J_{P-H} = 10$ Hz). It appears that the chemical shift of the dimetallated methylene bridge protons is not diagnostic for the presence or absence of a metal–metal bond since that observed in the present species is at significantly lower field than those observed in the related species, $[M_2Cl_2(\mu\text{-}CH_2)(DPM)_2]$ (M = Pd, $\delta = 1.64$ ppm [7]; M = Pt, $\delta = 1.08$ ppm [6]) where no M–M bond is proposed, but lies within the range observed (5.97–10.68 ppm) in metal–metal bonded species [2]. The $^{31}P\{^1H\}$ NMR spectrum shows a resonance at 8.1 ppm typical of an AA'A''A'''XX' spin system with a splitting of 124.2 Hz between the two major peaks.

$[Rh_2Cl_2(\mu\text{-}CH_2)(\mu\text{-}HFB)(DPM)_2]$ crystallizes as golden-amber prisms with 4/m diffraction symmetry in space group $P4_1$, with $a = 21.334(3)$ Å, $c = 14.574(2)$ Å, $V = 6633$ Å^3 and $Z = 4$. Intensity data were collected on an automated Nonius CAD4 diffractometer using graphite monochromated MoKα X-radiation, to $2\theta = 55.0^\circ$. Of the 9129 reflections

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TABLE I. Selected Bond Distances (Å) and Angles (deg).

Atoms	Distance	Atoms	Distance	Atoms	Distance
Rh(1)–C(1)	2.05(1)	Rh(1)–Cl(1)	2.441(3)	C(4)–C(5)	1.51(2)
Rh(2)–C(1)	2.07(1)	Rh(2)–Cl(2)	2.422(4)	Rh–P(av)	2.345(4)
Rh(1)–C(3)	1.97(1)	C(3)–C(4)	1.34(1)	Rh(1)··Rh(2)	3.464(1)
Rh(2)–C(4)	2.03(1)	C(2)–C(3)	1.52(2)		

Atoms	Angle	Atoms	Angle	Atoms	Angle
Rh(1)–C(1)–Rh(2)	114.5(5)	C(1)–Rh(1)–C(3)	91.0(5)	Rh(2)–C(4)–C(3)	119.9(9)
Cl(1)–Rh(1)–C(1)	110.6(3)	C(1)–Rh(2)–C(4)	90.6(5)	Rh(1)–C(3)–C(2)	114.2(9)
Cl(2)–Rh(2)–C(1)	106.9(4)	P(1)–Rh(1)–P(3)	171.7(1)	Rh(2)–C(4)–C(5)	113(1)
Cl(1)–Rh(1)–C(3)	158.4(4)	P(2)–Rh(2)–P(4)	171.8(2)	C(2)–C(3)–C(4)	122(1)
Cl(2)–Rh(2)–C(4)	162.5(3)	Rh(1)–C(3)–C(4)	124(1)	C(3)–C(4)–C(5)	128(1)

measured, 3669 were unique and observed and were used in the solution and refinement of the structure, which was solved by conventional Patterson and Fourier methods and refined by full matrix, least-squares techniques to R = 0.038 and R_w = 0.045. The carbon atoms of the phenyl rings were refined as rigid groups having individual isotropic thermal parameters and C–C distances of 1.392 Å, while all other non-hydrogen atoms were refined anisotropically. Although all hydrogen atoms have been located in Fourier maps they have not been included at the present stage of refinement. A perspective view of the molecule together with the numbering scheme used is shown in Fig.1 and some relevant bond lengths and angles are given in Table I.

As suggested by the spectral parameters, the methylene group has inserted into the Rh–Rh single bond of *2* yielding the symmetric methylene-bridged species *1*. The geometry of this species is very similar to that of the carbonyl analogue, $(Rh_2Cl_2(\mu\text{-Co})(\mu\text{-DMA})(DPM)_2]$ (*3*) (DMA = dimethylacetylene-dicarboxylate), which is one of the very few complexes containing a bridging carbonyl group without a metal–metal bond [9]. The product of direct insertion of a methylene fragment into a M–M single bond is not expected to be stable under most circumstances since the resulting binuclear species would be held together by only the methylene bridge. However, in the presence of other bridging groups such as DPM, which hold the metals in close proximity, the CH_2-bridged species lacking a metal–metal bond can be stable. Significantly, the analogous bridging ketonic carbonyl ligand has only been observed with accompanying bridging DPM or DAM (DAM = $Ph_2AsCH_2AsPh_2$) ligands [9, 11, 12].

As in compound *3* the long Rh–Rh separation in the title complex (3.464(1) Å) suggest no significant metal–metal interaction; this separation is much longer than the Rh–Rh single bonded distance of 2.7447(9) Å observed in the precursor (*2*). The

rhodium–methylene distances of 2.05(1) and 2.07(1) Å are not significantly different from those observed (2.029(4), 2.055(4) Å) when the methylene bridge is accompanied by a rhodium–rhodium single bond [13]. However, the present distances are significantly larger than the rhodium–carbonyl distance (1.977(4) Å) in *3*. This difference is somewhat greater than that expected on the basis of covalent radius differences between the sp^2 carbonyl carbon (0.73 Å) and the sp^3 methylene carbon (0.772 Å) and may reflect the π-acceptor capability of the carbonyl group; the sp^3 methylene group has no available orbitals for π-bonding. As a result of the larger Rh–C distances in *1* the Rh–Rh separation is greater than that in *3* (3.3542(9) Å) in spite of the smaller Rh–C–Rh angle at the methylene group (114.5(5)°) than at the carbonyl group (116.0(4)°).

In all previous methylene bridged compounds the M–CH$_2$–M angles have been observed within the range 81 ± 7° [2], whereas the present species has a Rh–CH$_2$–Rh angle of 114.5(5)°. This significantly larger angle has arisen as a result of the non-bonded metals allowing the CH_2 group to assume nearly its idealized sp^3 hybridization, in contrast with the metal–metal bonded cases where the M–CH$_2$–M angle is dictated by the close metal–metal separations. In the present case the Rh–CH$_2$–Rh angle is in fact greater than the value expected for sp^3 hybridization probably as a result of a compromise between the geometrical demands of the bridging methylene and acetylene groups; the latter tends to lengthen the Rh–Rh separation and widen the Rh–CH$_2$–Rh angle.

The coordinated acetylene moiety bears a close resemblance to those in the starting material *2* and the carbonyl analogue *3* and can be formulated as a *cis*-dimetallated olefin. As a consequence the C(3)–C(4) distance is consistent with a C=C double bond and the angles about C(3) and C(4) are all close to the 120° expected for sp^2 hybridiza-

tion. The average rhodium–acetylene distance of 2.00(1) Å is in good agreement with the analogous distances in *2* (1.996(9) Å) and *3* (2.004(6) Å) and differs from the rhodium–methylene distances by approximately the difference in the carbon sp^2 and sp^3 covalent radii (*vide supra*).

The structural characterization of this complex offers unambiguous confirmation that methylene-bridged species can be synthesized without accompanying metal–metal bonds. It also reemphasizes the ability of bridging DPM and DAM groups to stabilize unusual ligand geometries and bonding modes by holding the metals at the required separation. The synthetic route employed demonstrates that insertion of a methylene moiety into a metal–metal single bond is not confined to the chemistry of platinum. It is now of interest to determine whether the chemistry of this methylene group differs significantly from that of the more conventional bridging methylene groups which are accompanied by metal–metal bonds. To this end a detailed investigation of the chemistry of this species is now underway.

Acknowledgements

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