

Communications

Site-Selective Dihydrogen Addition to a Trirhodium Chain. Preparation and Structure of $[\text{Rh}_3(\mu\text{-}(\text{Ph}_2\text{PCH}_2)_2\text{PPh})_2(\text{H})_2(\text{CO})_2(\mu\text{-Cl})_2][\text{BPh}_4]$

Sir:

Despite the considerable attention given to the addition of small molecules and ions to binuclear, phosphine-bridged complexes,¹ particularly those of the A-frame class, no examples of dihydrogen addition to the $\text{Rh}_2(\mu\text{-dpm})_2$ (dpm is bis(diphenylphosphino)methane) core have been isolated and structurally characterized. The hydride complexes of this unit that have been made have been prepared by Rh-Rh bond protonation or by hydride addition.²⁻⁴ Here we describe dihydrogen addition to related trinuclear rhodium complexes with bis((diphenylphosphino)methyl)phenylphosphine (dpmp) bridges^{5,6} and point out several structurally significant features of the product.

Storage of a dichloromethane solution of $[\text{Rh}_3(\mu\text{-dpmp})_2(\mu\text{-CO})(\text{CO})(\mu\text{-Cl})\text{Cl}][\text{BPh}_4]^5$ under 1 atm of dihydrogen for 12 h produces a red solution from which red-orange crystals of $[\text{Rh}_3(\mu\text{-dpmp})_2(\text{H})_2(\text{CO})_2(\mu\text{-Cl})_2][\text{BPh}_4]^7$ can be isolated in 80-90% yield by the gradual addition of diethyl ether. Treatment of $[\text{Rh}_3(\mu\text{-dpmp})_2(\text{CO})_3(\mu\text{-Cl})\text{Cl}][\text{BPh}_4]^6$ in dichloromethane with 10 atm of dihydrogen for 12 h gives the same product in somewhat lower (60-80%) yield.

The structure of the cation as determined by an X-ray crystallographic study is shown in Figure 1.⁸ Figure 2 shows some

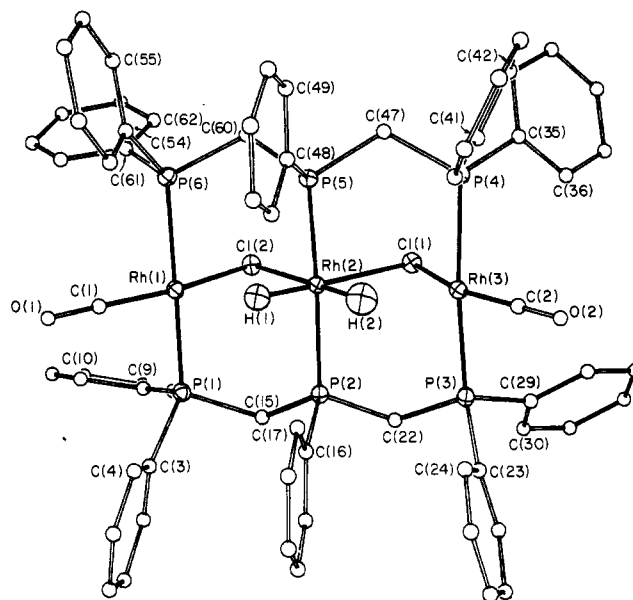


Figure 1. A perspective drawing of $[\text{Rh}_3(\mu\text{-dpmp})_2(\text{H})_2(\text{CO})_2(\mu\text{-Cl})_2]^+$.

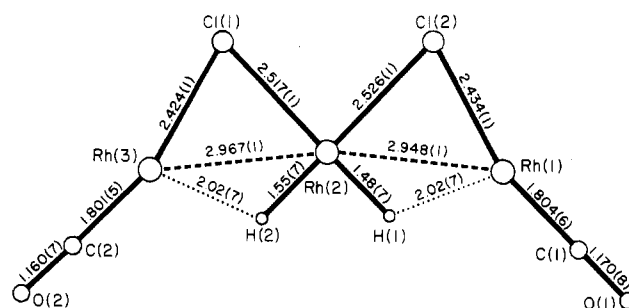


Figure 2. A drawing showing some dimensions within the planar section of the cation. Some interatomic angles (deg): H(1)-Rh(2)-H(2), 90(3); H(1)-Rh(2)-Cl(2), 91(3); H(2)-Rh(2)-Cl(1), 91(3); Cl(1)-Rh(2)-Cl(2), 88.1(1); P(5)-Rh(2)-Cl(1), 95.0(1); P(5)-Rh(2)-Cl(2), 94.6(1); P(2)-Rh(2)-Cl(1), 94.8(1); P(2)-Rh(2)-Cl(2), 94.3(1); C(1)-Rh(1)-Cl(2), 164.1(2); C(2)-Rh(3)-Cl(1), 163.8(2); Rh(1)---Rh(2)---Rh(3), 168.1(1); Rh(2)-Cl(1)-Rh(3), 73.8(1); Rh(1)-Cl(2)-Rh(2), 72.9. Rh-P distances (Å): Rh(1)-P(1), 2.324(1); Rh(1)-P(6), 2.327(1); Rh(2)-P(2), 2.276(1); Rh(2)-P(5), 2.278(1); Rh(3)-P(3), 2.330(2); Rh(3)-P(4), 2.327(1).

of the dimensions within the planar $\text{Rh}_2(\text{H})_2(\text{CO})_2\text{Cl}_2$ section. As usual in complexes of this type, the triphosphines are aligned trans to one another. The chloride ligands are bridging, and the carbonyl groups are terminal. The overall geometry can be considered as two A-frame units placed side by side. Although there is no crystallographically imposed symmetry to the cation, it has effective C_{2v} symmetry with the C_2 axis bisecting the Cl-

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- ¹H NMR: hydride, $\delta = -13.3$, $J(\text{Rh}(2)\text{-H}) = 24.7$ Hz, $J(\text{Rh}(1$ or $3)\text{-H}) = 10.9$ Hz, $J(\text{P-H}) = 8$ Hz; methylene, $\delta = 3.0, 3.8$, $J(\text{H-H}) = 12.7$ Hz. ¹³P NMR: broad multiplet at 27 ppm. ¹³C NMR: $\delta = 190.0$, $J(\text{Rh-C}) = 80.6$ Hz. IR: $\nu(\text{CO}) = 1963$ cm^{-1} , KCl wafer. UV-vis: $\lambda_{\text{max}} = 472$ nm ($E = 22500$).
- Red-orange single crystals of $[\text{Rh}_3(\mu\text{-dpmp})_2(\text{H})_2(\text{CO})_2(\mu\text{-Cl})_2][\text{BPh}_4]$ were grown by diffusion of ethyl ether into a dichloromethane solution of the complex. They belong to the space group $P2_1/n$ (No. 14) with $a = 14.498$ (2) Å, $b = 22.077$ (3) Å, $c = 28.353$ (3) Å, $\beta = 99.86$ (1)°, and $Z = 4$ at 140 K. Refinement yields $R = 0.049$, $R_w = 0.054$ for 12079 reflections with $I > 3\sigma(I)$ and 558 parameters. The hydrides were refined and were well-behaved.

(1)-Rh(2)-Cl(2) and H(1)-Rh(2)-H(2) angles. The positions of the hydride ligands are significant for a number of reasons.

The hydrides are primarily localized on Rh(2). The Rh(2)-H distances (1.55 (7), 1.48 (7) Å) are typical for terminal hydride ligands.^{9,10} The coordination geometry at Rh(2) is regular six-coordinate with bond angles of 88-95° between cis ligands. Consequently, single site oxidative addition of dihydrogen appears to have occurred. Notice that the hydrides are bound to a rhodium center lacking a carbonyl ligand. Since Rh(PPh₃)₃Cl forms a stable adduct with dihydrogen while Rh(PPh₃)₂(CO)Cl does not,¹¹ it appears that carbon monoxide ligands deactivate Rh(I) toward reaction with dihydrogen. The high trans effect of the hydride ligands has lengthened the Rh(2)-Cl distances relative to the Rh(1)-Cl and Rh(3)-Cl distances while the oxidation of Rh(2) has shortened the Rh(2)-P bonds relative to the Rh(1)-P and Rh(3)-P bonds.

There is some evidence for a semibridging interaction between the hydrides and the terminal rhodium atoms. The phosphorus-decoupled ¹H NMR spectrum shows a doublet of doublets with two Rh-H couplings. The larger (24.7 Hz) is assigned to the Rh(2)-H coupling while the smaller (10.9 Hz) is assigned to the Rh(1)-H(1) and Rh(3)-H(2) coupling. The observation of coupling to Rh(1) and Rh(3) should not be surprising. The hydride ligands lie directly above the planar Rh(CO)ClP₂ end groups, and the filled d_z and empty p_z orbitals of Rh(1) and Rh(3) are directed toward these hydrides. Nevertheless, the interactions must be weaker than those that are present in normal bridging hydrides. The Rh(2)···Rh(1) and Rh(2)···Rh(3) distances are considerably longer than the Rh-Rh distances in other complexes with more or less symmetrically bridging hydrides including the following (Å). [Rh₂(μ-dpm)₂(μ-H)(μ-CO)(CO)₂]⁺: Rh-Rh, 2.731 (2); Rh-H, 1.97 (11), 1.75 (11).² [Rh₂(μ-dpm)₂(μ-H)(μ-CO)Cl]₃: Rh-Rh, 2.7464 (7); Rh-H, 1.76 (6), 1.65 (6).⁴ Rh₃(μ-H)₃[P(OMe)₃]₆: Rh-Rh, 2.803 (7), 2.780 (6), 2.856 (8); Rh-H, 1.76 (3) average.¹² Rh₂(μ-H)₂(H)₂[P(NMe)₂]₄: Rh-Rh, 2.734 (1); Rh-H_{br}, 1.68 (3), 1.77 (3).⁹ Rh²(μ-H)₂[P(O-*i*-Pr)]₄: Rh-Rh, 2.65 (1); Rh-H, 1.805 (14), 1.812 (13).¹³ Also, the Rh(1)···H(1) (2.02 (7) Å) and Rh(3)···H(3) (2.02 (7) Å) distances are longer and the Rh(2)-H distances are shorter than those in normal hydride bridges.¹⁴

Site-selective (that is, addition at a single metal center) dihydrogen addition to polynuclear rhodium complexes appears to be emerging as a significant characteristic of these species. Other examples include the addition to (Ph₃P)₂Rh(μ-Cl)₂Rh(PPh₃)₂ to form (Ph₃P)₂Rh(μ-Cl)₂Rh(H)₂(PPh₃)₂¹⁵ and to ((Me₂N)₃P)₂Rh(μ-H)₂Rh(P(NMe)₂)₃ to form ((Me₂N)₃P)₂Rh(μ-H)₂Rh(H)₂(P(NMe)₂)₃.⁹ Examples of multicentered dihydrogen addition are at present limited to two-centered addition to sulfur-bridged, diiridium complexes.^{16,17} In contrast, multicentered dihalogen addition to polynuclear complexes appears to be a much more widespread phenomenon.^{1,18}

The observation of site-selective dihydrogen addition is particularly noteworthy because it suggests that polynuclear catalysts can be designed with rhodium centers specifically for activating dihydrogen and with other metal centers for binding and activating a second substrate.

The reaction chemistry of [Rh₃(μ-dpmp)₂(H)₂(CO)₂(μ-Cl)₂]⁺ and related hydrides is under investigation. [Rh₃(μ-dpmp)₂(H)₂(CO)₂Cl]₂[BPh₄] is a catalyst for hydrogenation of terminal olefins. It hydrogenates 1-phenyl-2-propyne catalytically to *cis*-1-phenyl-2-propene. With carbon monoxide it reacts by apparent dihydrogen loss to form [Rh₃(μ-dpmp)₂(CO)₃(μ-Cl)-Cl]₂[BPh₄] in 90% yield.

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Registry No. [Rh₃(μ-dpmp)₂(μ-CO)(CO)(μ-Cl)Cl]₂[BPh₄], 95045-36-6; [Rh₃(μ-dpmp)₂(CO)₃(μ-Cl)Cl]₂[BPh₄], 84774-75-4; [Rh₃(μ-dpmp)₂(H)₂(CO)₂(μ-Cl)₂][BPh₄]₂·3CH₂Cl₂, 98735-48-9; 1-phenyl-2-propyne, 10147-11-2; dihydrogen, 1333-74-0.

Supplementary Material Available: Listings of atomic fractional coordinates, thermal parameters, bond lengths, and bond angles for [Rh₃(μ-dpmp)₂(H)₂(CO)₂(μ-Cl)₂][BPh₄]₂·3CH₂Cl₂ (7 pages). Ordering information is given on any current masthead page.

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Photoemission from Tungsten Alkylidyne Complexes in Fluid Solution

Sir:

Over the past 2 decades there has been much interest in organometallic species that luminesce at room temperature in fluid solution upon excitation with visible irradiation. Such species have low-lying excited states, which may allow utilization of optical energy in the preparation of useful chemical products.¹ Despite this interest there exists a scarcity of such species. In most cases where the desired luminescence is observed, it has been associated with a charge-transfer transition involving metal *dπ* electrons and the π* orbital of a ligated aromatic diimine.² To the best of our knowledge emission in fluid solution from a species containing a metal-carbon multiple bond has not been noted in the literature. We report here on a new class of luminescent organometallic complexes, containing a metal-alkylidyne linkage and having the general stoichiometry [XW(CO)₂L₂(CR)] (where X = halide, L = donor ligand, and R = phenyl),³ which yield emission in fluid solution upon visible excitation. We find the luminescent properties of these complexes to be very dependent on both the nature of the R group and the L ligand. This dependence leads us to the conclusion as discussed below that the luminescent state is associated with the alkylidyne ligand.

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