$[(\mu_4\text{-H})Rh_4(PNNP)_2(CO)_4]^+$: A Novel Hydride Bridging Mode**

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Bridging hydride is a key structural feature of transition metal cluster compounds[1] and a number of cluster compounds containing doubly (μ) and triply (μ_3) bridging hydrido ligands are known. Compounds with a hydrido ligand bridging more than three metal atoms, however, are still rare (Figure 1). To the best of our knowledge, only one example each for a μ_4- and μ_5-hydride complex has been reported and only the structural types **A**–**C** have been characterized for μ_n-H complexes ($n \geq 4$).[2] In addition, the multiply bridging hydrido ligands in all the previous examples are associated with cluster frameworks as in **A**–**C**. During the course of our study on the interaction of dinuclear species with hydrosilanes,[3] we have encountered a novel **D**-type μ_4-hydrido ligand, which holds four isolated metal centers together through M–H interactions. This work reveals that a cluster framework supported by metal–metal bonds is not essential for a multiply bridging hydride.

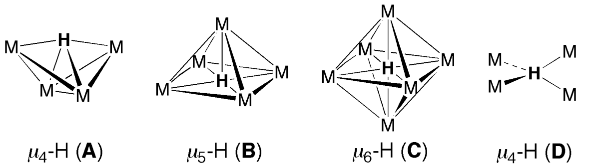
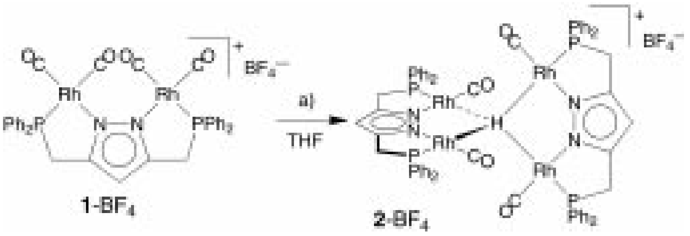

μ_4-H (**A**) μ_5-H (**B**) μ_6-H (**C**) μ_4-H (**D**)

Figure 1. Structural types for compounds containing hydrido ligands bridging more than three metal centers.

When a THF solution of $[Rh_2(PNNP)(CO)_2]BF_4$ (**1**BF_4; PNNP = 3,5-bis(diphenylphosphinomethyl)pyrazolate)[4] was treated with a hydrosilane, such as $HSiEt_3$, $HSiMe_2Ph$, and H_2SiPh_2 (Scheme 1), the purple product **2**BF_4 precipitated from the mixture; the ^1H NMR spectrum of **2**BF_4 shows a complicated hydride resonance signal (Figure 2a). The intensity of this hydride signal and an electrospray ionization mass spectrometry (ESI-MS) spectrum suggest the formation of a dimeric species (m/z: 1451, the molecular ion peak for **2**) formulated as $[(H)Rh_4(PNNP)_2(CO)_4]BF_4$ (**2**BF_4). The same product was obtained irrespective of the hydrosilane used, which suggests that the hydrosilane serves as a hydride donor; the reaction of **1**BF_4 with $[D_2]SiPh_2$ resulted in selective deuteration of the bridging hydride in $[D_1]$**2**BF_4 as confirmed by ^1H NMR spectroscopy and ESI-MS. For the $[Rh_2(PNNP)(CO)_2]$ moiety of **2**, only a single set of signals arising from the CH_2PPh_2 (^1H, ^{13}C, and ^{31}P NMR spectroscopy), pyrazolyl (^1H and ^{13}C NMR spectroscopy), and CO moieties (infrared (IR) and ^{13}C NMR spectroscopy) was observed suggesting a four-fold symmetrical structure. In addition, the complicated hydride signal was successfully analyzed and found to result from coupling with four equivalent Rh–P units ($^1J(Rh,H) = 31.2$ Hz, $^2J(P,H) = 13.6$ Hz; Figure 2b). The spectral data are consistent with a tetrarhodium complex with a tetrahedral or square planar Rh_4 array linked by a symmetrically bridging μ_4-hydrido ligand, $[(\mu_4\text{-H})Rh_4(PNNP)_2(CO)_4]BF_4$ (**2**BF_4).



Scheme 1. a) $HSiEt_3$, $HSiMe_2Ph$, or H_2SiPh_2.

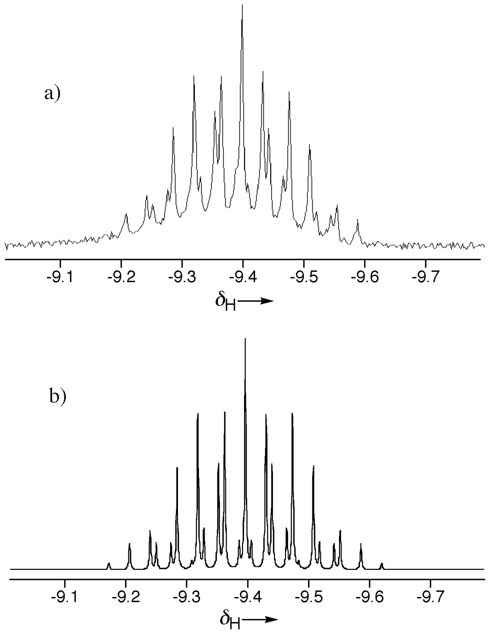


Figure 2. 400 MHz ^1H NMR spectra of **2**BF_4 (hydride region). a) Observed spectrum (in CD_2Cl_2); b) simulated spectrum, $\delta_H = -9.39$ ($J(Rh,H) = 31.2$, $J(P,H) = 13.6$ Hz).

Despite many attempts a single crystal of **2**BF_4 could not be obtained, but anion exchange with $NaBPh_4$ afforded $[(\mu_4\text{-H})Rh_4(PNNP)_2(CO)_4]BPh_4$ (**2**BPh_4) as deep purple plates, suitable for X-ray crystallography (Figure 3).[5] The two $[Rh_2(PNNP)(CO)_2]$ subunits are arranged almost perpendicular to each other to form a Rh_4 tetrahedron, and the hydride atom (H1) refined isotropically can be located in the middle of the Rh_4 tetrahedron as is consistent with the spectral data. Thus **2**BPh_4 is found to be the second example of a structurally characterized $(\mu_4\text{-H})M_4$ complex, after the $[(\mu_4\text{-H})W_4(OCH_2tBu)_{12}]^-$ ion[2a,b] in which the μ_4-hydrido ligand is supported on a butterfly M_4 cluster framework (type **A**; Figure 1).

The Rh_4 tetrahedron in **2** is distorted to a small extent; the Rh···Rh separations between the two subunits are in the

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[**] PNNP = 3,5-bis(diphenylphosphanylmethyl)pyrazolate.

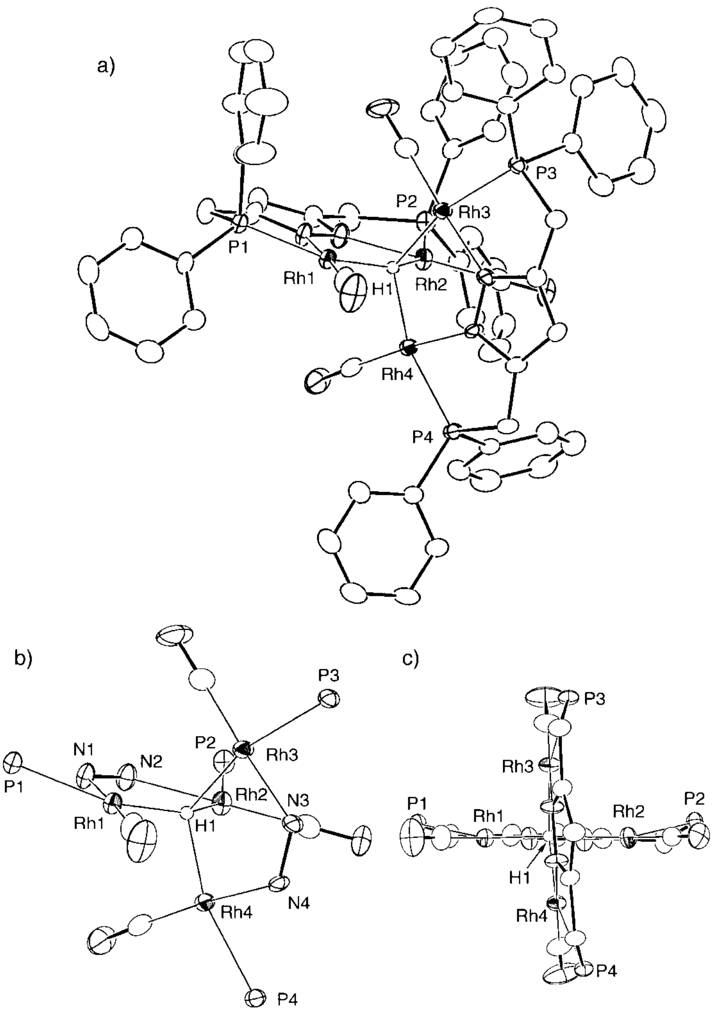

Figure 3. a) Molecular structure of the cation of $\mathbf{2}BPh_4$ thermal ellipsoids set at the 30 % probability level. b) An expanded view of the core. c) A side view of the core.

range of 2.89 – 3.10 Å (Rh1 ⋯ Rh3 2.9083(9), Rh1 ⋯ Rh4 2.8890(7), Rh2 ⋯ Rh3 3.1022(6), Rh2 ⋯ Rh4 2.8969(8); Rh1 ⋯ Rh2 3.4730(8), Rh3 ⋯ Rh4 3.4153(6) Å) and the H1 atom is not equidistant from the four Rh centers (Rh–H 1.70 – 2.05 Å). The side view (Figure3 c) shows that, in both of the $[Rh_2(PNNP)(CO)_2]$ subunits, the two five-membered $RhPC_2N$ chelate rings fused to the central pyrazolyl ring are slightly folded in the same direction leading to envelope-type conformations. This folding causes distortion in the solid state but fast flipping of the chelate rings in solution should account for the apparently symmetrical configuration suggested by the spectral features. No change in the ^1H (Rh–H) and ^{31}P NMR spectroscopy signals was detected upon cooling to −80 °C. The Rh ⋯ Rh separations are slightly longer than the sum of the atomic radii of Rh (2.68 Å). If some Rh–Rh bonding interaction is present, it should induce distortion of the square-planar coordination geometry of the d^8 metal center Rh^I. However, the four Rh coordination planes are virtually planar (sum of the inter-ligand angles: 360(3)°), thus the Rh–Rh bonding interaction is negligible and the close Rh – Rh contacts result from the very small hydrogen atom linking the four rhodium atoms. Thus the hydrido ligand in complex **2** is characterized as the first example of a **D**-type μ_4-hydride in a discrete molecule (cation). The bridging hydrido ligand encapsulated in the Rh_4 tetrahedron is shielded from the outside and, accordingly, $\mathbf{2}BF_4$ is stable in CH_2Cl_2.

The μ_4-hydride complex $\mathbf{2}BF_4$ should be formed by a sequence of 1) initial hydride transfer from $HSiR_3$ to $\mathbf{1}BF_4$ to form the neutral dinuclear μ-hydride intermediate, $[(\mu\text{-}H)Rh_2(PNNP)(CO)_2]$, and 2) further interaction with another molecule of $\mathbf{1}BF_4$. The dissociation of the labile CO ligands *trans* to P centers in rhodium complexes has already been noted by Bosnich and co-workers,[4] thus, $\mathbf{1}BF_4$ forms a coordinatively unsaturated species, which is trapped by the hydrido ligand in $[(\mu\text{-}H)Rh_2(PNNP)(CO)_2]$ to give $\mathbf{2}BF_4$. Note that reaction of $\mathbf{1}BF_4$ with $LiHBEt_3$ or $NaBH_4$ did not afford $\mathbf{2}BF_4$ but a mixture of unidentified products.

Although the metal part of **2** is electron deficient (with 58 valence electrons: 64 valence electrons expected ($16e^- \times 4$)), such an unsaturated electronic structure must be kinetically stabilized by the bulky PNNP ligands surrounding the Rh_4 tetrahedron. Preliminary extended-Hückel molecular orbital (EHMO) analysis reveals that the tetranuclear structure is formed by interaction of the hydride orbital with the LUMO of the tetranuclear $[Rh_4(PNNP)_2(CO)_4]^{2+}$ fragment, where the four σ-type rhodium d orbitals of the in-phase combination are projected toward the center of the Rh_4 tetrahedron, that is, towards the position occupied by the μ_4-hydrido ligand. A similar MO feature was noted for the μ_4-H tetratungsten cluster compound mentioned above.[2a,b]

In conclusion, the present study reveals that support by a metal – metal bonded cluster framework is not essential for a multiply bridging hydride (μ_n-H: $n \geq 4$). In all the previous examples (**A** – **C**; Figure 1) the multiply bridging hydrido ligand appears to be protected by the cluster framework, whereas, in the present system, the hydride is not accommodated in a cavity formed by the cluster framework but binds the four isolated rhodium centers (which are not connected by metal – metal bonds) together. The binding force is strong enough to bring the Rh centers close enough together so that the distances between them are comparable to the sum of the atomic radii. The unique feature of the $[Rh_2(PNNP)(CO)_2]^+$ fragment with the two vacant *cis*-oriented coordination sites is now under further study.

Experimental Section

$\mathbf{2}BF_4$: $\mathbf{1}BF_4$ (258 mg, 0.272 mmol) was added to a THF solution (20 mL) of $HSiEt_3$ (40 µL, 0.25 mmol) and the resultant mixture was stirred at ambient temperature until gas evolution ceased (ca. 1.5 h). The supernatant solution was removed by cannula and the remaining purple precipitate was washed with a minimum amount of THF and dried under reduced pressure. $\mathbf{2}BF_4$ (119 mg, 0.078 mmol, 57 % yield) was obtained as deep purple powder. Crystallization from CH_2Cl_2/hexane afforded deep purple plates. ^1H NMR (400 MHz, CD_2Cl_2, 25 °C): $\delta = -9.39$ (quintet of quintets, $^1J(Rh,H) = 31.2$ Hz, $^2J(P,H) = 13.6$ Hz, 1H; μ_4-H), 3.68 (d, $^2J(P,H) = 10$ Hz, 8H; CH_2P), 6.24 (s, 2H; 4-pyrazolyl ring proton), 7.4 – 7.7 (m, 40H; Ph); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 25 °C): $\delta = 57.41$ (d, $J(Rh,P) = 200$ Hz); $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, 25 °C): $\delta = 31.8$ (d, $^1J(P,C) = 29$ Hz; CH_2P), 100.3 (t, $J = 12$ Hz; 4-pz), 129.5 (d, $^3J(P,C) = 13$ Hz; *m*-Ph), 131.7 (s; *p*-Ph), 132.9 (d, $^2J(P,C) = 13$ Hz; *o*-Ph), 133.0 (d, $^1J(P,C) = 50$ Hz; *ipso*-Ph), 155.4 (dd, $J = 9$, 4 Hz; 3,5-pz), 192.4 (dd, $^1J(Rh,C) = 62$, $^2J(P,C) = 11$ Hz; RhCO); IR (KBr): $\tilde{\nu} = 1983$ cm^{-1} (CO); ESI-MS: m/z: 1451 [M^+] for the cation (**2**).

2BPh$_4$: A THF/CH$_2$Cl$_2$ solution (1/1; 3 mL) of NaBPh$_4$ (42 mg, 0.12 mmol) was added to a THF/CH$_2$Cl$_2$ solution (1/1; 10 mL) of **2**BF$_4$ (100 mg, 0.06 mmol) and the mixture was stirred for 20 min. After concentration to ca. 6 mL hexane (8 mL) was added to form precipitates, which were collected by filtration. The solid was dissolved in CH$_2$Cl$_2$ (1.5 mL). Hexane (1 mL) was added and purple **2**BPh$_4$ (80 mg, 0.045 mmol, 75 % yield) was obtained by crystallization at -20 °C.

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[5] Crystal data for **2**BPh$_4\cdot$2CH$_2$Cl$_2\cdot$0.5hexane: $C_{91}H_{82}BN_4O_4P_4Cl_4Rh_4$, $M_W = 1983.74$, triclinic, space group $P\bar{1}$, $a = 17.8753(14)$, $b = 18.8768(13)$, $c = 13.7743(10)$ Å, $\alpha = 103.703(3)$, $\beta = 97.179(5)$, $\gamma = 105.748(5)$°, $V = 4256.1(6)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.548$ g cm^{-3}, $\mu = 1.016$ cm^{-1}, $R_1 = 0.0664$ (on F^2) for the 11879 unique data ($wR_2 = 0.1792$ for all 16104 data) with $F > 4\sigma(F)$ and 968 parameters. X-ray diffraction measurements were made on a Rigaku RAXIS IV imaging plate area detector with graphite-monochromated Mo$_{K\alpha}$ radiation at -60 °C. The structure was solved by a combination of the direct methods (SHELXS86) and DIRDIF. Least-squares refinements were carried out using SHELXL97 linked to teXsan (Single Crystal Structure Analysis Package, ver.1.11, Rigaku Corporation, Tokyo **2000**). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-159668. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Double Photoionization of Dimethylaminobenzonitrile in Solution: A Three-Quantum Process with Intervening Chemical Step[**]

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Photoionization in solution is a compelling subject of investigation because of the vast importance of the hydrated electron $e_{aq}^{\bullet -}$ for chemical and biological processes.[1] At wavelengths greater than about 300 nm, more than one photon is usually needed to eject an electron from a stable molecule. This is normally realized by an absorption–absorption sequence (two consecutive absorption steps), where the second photon ionizes an electronically excited state of the substrate.

As we recently demonstrated, the insertion of an electron-transfer step between the two absorption processes can greatly facilitate two-photon ionization.[2] With this variant, the second photon ionizes the radical anion resulting from electron-transfer quenching of the excited substrate. Experimental evidence obtained so far seems to indicate that at least for aromatic ketones and quinones the actual photoionization step is intrinsically more efficient by an order of magnitude or more for the radical anion than for the excited nπ* triplet state.[2d, 3]

Up to now, this mechanistic variant has only been explored with intermolecular quenching. When both absorption steps are to occur during the same laser flash, that is, typically within a few nanoseconds, this puts considerable constraints on the chemical system: even in the case of a diffusion-controlled electron transfer disproportionately high quencher concentrations must still be employed.[2d] The use of *intra*molecular charge transfer (ICT) is an obvious approach to overcome this difficulty. On the basis of the above experimental observation, one would expect photoionization of an excited state to be the more facile the greater its charge transfer (CT) character is.

Dimethylaminobenzonitrile (DMABN) is a classical ICT compound as far as its first excited singlet state is concerned. However, with regard to the lowest triplet state T_1 the situation is less clear. From an analysis of its deactivation pathways[4] and from the absence of an appreciable volume change in laser-induced optoacoustic spectroscopy[5] it was inferred that T_1 does not possess a pronounced CT character. In contrast, the results of time-resolved infrared measurements indicate that in T_1 a substantial negative charge is located on the cyano group, and it was proposed that there might be two closely lying triplet states, a CT and a non-CT one, with an equilibrium between them.[6]

DMABN can be photoionized in liquid solution at 266 and 308 nm; from a quadratic intensity dependence of the yield of

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