Communications

Mono- and Dihydrido-Bridged Tungsten–Platinum Complexes

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Summary: The preparation and X-ray crystal structure of the monohydrido-bridged cation $[(\eta^5\text{-}C_5H_5)_2(H)W(\mu\text{-}H)Pt(Ph)(PEt_3)_2]^+$ and of the dihydrido-bridged cation $[(\eta^5\text{-}C_5H_5)_2W(\mu\text{-}H)_2Pt(Ph)(PEt_3)]^+$ are reported. Structural and NMR data show that the W–Pt interaction is considerably stronger in the dihydrido than in the related monohydrido-bridged species.

Studies of complexes containing M–H$_n$–M′ bridging units have shown that the M–M′ separation is related to the number of bridging hydrides, *n*.[1] We report here synthetic, NMR, and X-ray structural data on two related hydrido-bridged tungsten–platinum compounds with widely different M–M separations due to a difference in number of bridging hydrogen atoms.

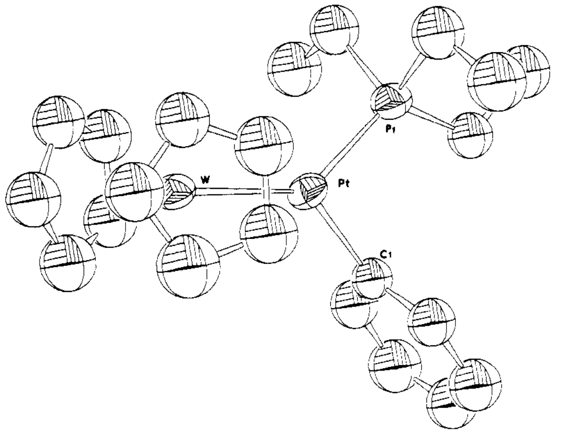
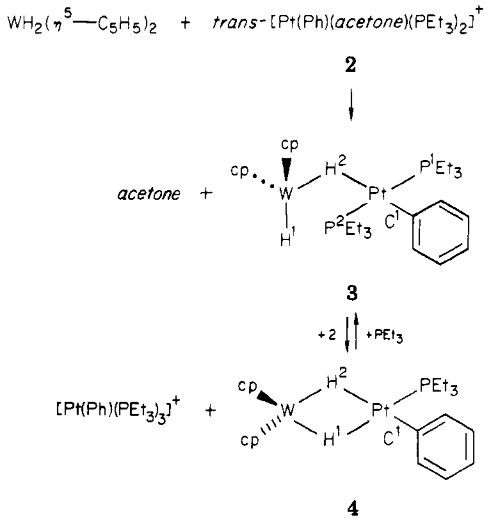


Figure 1. An ORTEP view of $[(\eta^5\text{-}C_5H_5)_2W(\mu\text{-}H)_2Pt(Ph)(PEt_3)][BPh_4]$, **4**.

Scheme I



The reaction of $WH_2(\eta^5\text{-}C_5H_5)_2$,[2] **1**, with the cation $[PtPh(acetone)(PEt_3)_2]^+$,[3] **2**, at −78 °C, gives the bimetallic species $[(\eta^5\text{-}C_5H_5)_2(H)W(\mu\text{-}H)Pt(Ph)(PEt_3)_2]^+$, **3**, which was characterized as its $[BF_4]^-$, **3a**, and $[BPh_4]^-$, **3b**, salts. However, the reaction of 1 equiv of **1** with 2 equiv of **2** gives $[Pt(Ph)(PEt_3)_3]^+$[4] and the binuclear species $[(\eta^5\text{-}C_5H_5)_2W(\mu\text{-}H)_2Pt(Ph)(PEt_3)]^+$, **4**, which was characterized as its $[BPh_4]^-$ salt. These reactions are summarized in Scheme I. The binuclear species were characterized by X-ray diffraction,[5,6] NMR spectroscopy, chemical analysis, and IR spectroscopy.[7] The overall geometry of **4** is shown in Figure 1, and the relevant bonding parameters are given in Table I. The coordination geometry at the platinum atom can be described as square-planar with one phenyl group, one phosphine, in mutually cis positions (P–Pt–C(1) = 88.2 (5)°), and two bridging hydride ligands whose

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(3) Clark, H. C.; Fiess, P. L.; Wong, C. S. *Can. J. Chem.* **1977**, *55*, 177.

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(5) Compound **3b** is triclinic of space group $P\bar{1}$ with the following unit-cell constants: a = 11.150 (3) Å, *b* = 19.842 (3) Å, *c* = 22.322 (4) Å, α = 88.1 (1)°, β = 88.2 (1)°, γ = 76.4 (1)° (least-squares refined values obtained for 25 high order reflections); *Z* = 4; *V* = 4797.3 (2) Å^3; ρ_{calcd} = 1.583 g cm^{-3}. Data were collected on a Philips PW 1100 diffractometer up to a $\theta_{max} \leq 20°$ at room temperature (Mo K$\bar{\alpha}$ graphite monochromated radiation) using $\omega/2\theta$ scan (scan speed 0.05° s^{-1} and a constant scan width of 1.10°). A total of 7727 independent reflections were collected of which 6325 were considered as observed (having $I_{net} \geq 3\sigma(I)$) and subsequently used for the solution and refinement of the structure. The structure was solved by Patterson and Fourier methods and refined by block-diagonal least squares to the present conventional *R* factor of 0.057 (for the observed reflections; R_w = 0.060) using anisotropic temperature factors for the P, Pt, and W atoms and isotropic thermal parameters for the others. Scattering factors were taken from ref. 8. The correction for the real part of the anomalous dispersion was taken into account.

(6) Compound **4** is triclinic of space group $P\bar{1}$ with the following unit-cell constants *a* = 15.759 (3) Å, *b* = 14.045 (3) Å, *c* = 9.467 (2) Å, α = 89.9 (2)°, β = 107.0 (2)°, γ = 88.8 (2)° (least-squares refined values obtained from 20 high-order reflections); *Z* = 2; *V* = 2004.3 (4) Å^3; ρ_{calcd} = 1.699 g cm^{-3}. Data were collected as for compound **3b** up to a $\theta_{max} \leq 21.0°$. A total of 3140 independent reflections were collected; after data reduction 1650 were considered as observed (having $I_{net} \geq 3\sigma(I)$ and subsequently used in the solution and refinement of the structure, carried out as for **3b**, to the present R factor of 0.045 (for the observed reflections; R_w = 0.053). In the final difference Fourier map two peaks are assignable to the bridging hydrides. However, their positions did not refine satisfactorily.

(7) Compound **4** does not show any band assignable to vibrations involving the hydride ligands in the region 1600–2400 cm^{-1} while **3a** shows a very broad absorption in the region 1600–1850 cm^{-1} as well as a medium-weak band at 1960 cm^{-1}.

(8) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

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Table I. Selected Bond Distances (Å) and Angles (deg) for the Cations $[(\eta^5\text{-}C_5H_5)_2W(\mu\text{-}H)_2Pt(Ph)(PEt_3)]^+$, 4, and $[(\eta^5\text{-}C_5H_5)_2(H)W(\mu\text{-}H)Pt(Ph)(PEt_3)_2]^+$, 3b[a]

	4	3b[b]
W-Pt	2.663 (1)	3.501 (1)
Pt-P(1)	2.216 (5)	2.337 (5)
Pt-P(2)		2.332 (5)
Pt-C(1)[c]	2.01 (1)	2.03 (1)
W-C[d]	2.29 ± 0.04 (3)	2.30 ± 0.04 (2)
W-Pt-P(1)	137.80 (5)	90.4 (1)
W-Pt-P(2)		97.9 (1)
W-Pt-C(1)	134.0 (2)	169.0 (2)
P(1)-Pt-P(2)		170.6 (2)
P(1)-Pt-C(1)	88.2 (5)	87.6 (5)
P(2)-Pt-C(1)		85.0 (5)
Cp-W-Cp[e]	149.5 (6)	143.4 (6)

[a] Esd's on the last significant figure are given in parentheses. [b] This compound crystallizes with two independent molecules in the unit cell which, although chemically equivalent, are crystallographically independent. The data given here relate to molecule A (see Table SI). The only significant difference in the geometry of the two independent molecules is the W-Pt bond length which for molecule B is 3.440 (1) Å. A similar behavior has been observed in the anion $[(CO)_5M(\mu\text{-}H)M(CO)_5]^-$ (M = W[1] and Mo[13]) where the W···W separation changes with a change of counterion. These differences have been attributed to the influence of lattice effects on the binuclear framework.[1] [c] Carbon atom of the phenyl group directly bonded to platinum. [d] Average values, the ± sign refers to the root-mean-square deviation from the mean. [e] Cp denotes the center of gravity of the cyclopentadienyl group.

positions could not be reliably located on a difference Fourier map. The two cyclopentadienyl groups and the two bridging hydrides are tetrahedrally arranged around the tungsten atom. As expected for a square-planar arrangement of donor atoms around platinum, this plane and that defined by tungsten and the centers of gravity of the two cyclopentadienyl rings make a dihedral angle of 89.8°. Furthermore, the WCp_2 moiety is symmetrically placed with respect to the W-Pt axis as expected for the presence of two W-H-Pt bridges.

The W-Pt distance, 2.663 (1) Å, is quite short as the metal-metal distances in $[(Et_3P)_3(H)Ir(\mu\text{-}H)_2Pt(Ph)(PEt_3)][BPh_4]$,[9] **5**, and $[\eta^5\text{-}C_5H_5)_2W(\mu\text{-}H)_2Rh(PPh_3)_2][PF_6]$,[10] **6**, are 2.687 (2) and 2.721 (8) Å, respectively, while in $[Et_4N]_2[(CO)_4W(\mu\text{-}H)_2W(CO)_4]$,[11] **7**, it is 3.016 (1) Å. The Pt-P distance in compound **4** is rather short (2.216 (3) Å) and is comparable with that found in compound **5** (2.213 (6) Å). The solution NMR data are consistent with the solid-state structure. The ^1H NMR spectrum of **4** at ca. −30 °C shows the presence of two nonequivalent hydrides, $\delta(H^1)$ −14.1 and $\delta(H^2)$ −17.1, coupled to phosphorus ($^2J(^{31}P\text{-}^1H^1)$ = 59.6 Hz; $^2J(^{31}P\text{-}^1H^2)$ = 8.8 Hz), platinum ($^1J(^{195}Pt\text{-}^1H^1)$ = 727 Hz; $^1J(^{195}Pt\text{-}^1H^2)$ = 625 Hz), and tungsten ($^1J(^{183}W\text{-}^1H^1)$ = 99.1 Hz; $^1J(^{183}W\text{-}^1H^2)$ = 101.1 Hz). The $^2J(^1H^1\text{-}^1H^2)$ is not resolved and, given the line widths, it must be less than 5 Hz.

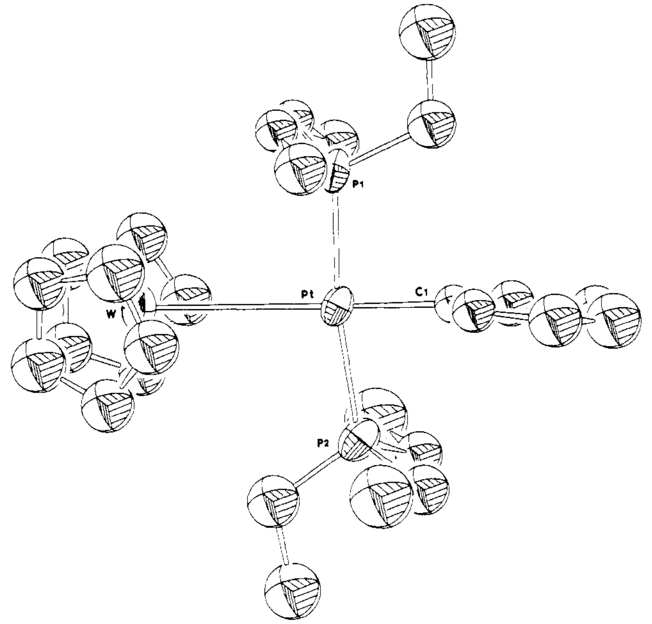

Figure 2. An ORTEP view of $[(\eta^5\text{-}C_5H_5)_2(H)W(\mu_2\text{-}H)Pt(Ph)(PEt_3)_2][BPh_4]$, **3b**.

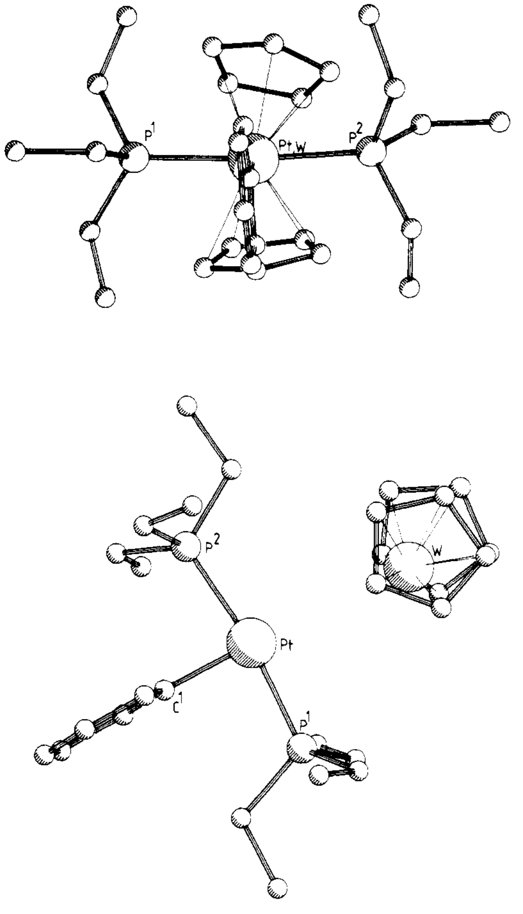

Figure 3.

The molecular structure of compound **3b** is shown in Figure 2, and a selection of bonding parameters are given in Table I. The most striking structural change observed between **4** and **3b**, i.e., upon coordinating a second phosphine to the platinum atom, is the lengthening of the W-Pt bond from 2.663 (1) in **4** to 3.501 (1) Å in **3b**. The W-Pt distance in **3b** is indicative of a weak W-Pt direct interaction in the solid state as (1) the Pt-Pt separation in $[(PEt_3)_2(Ph)Pt(\mu\text{-}H)Pt(Ph)(PEt_3)_2][BPh_4]$,[12] which contains only a single Pt-H-Pt bridge, is 3.238 (1) Å[11] and (2) the W-W separation in compounds containing a singly bridged W-H-W unit range from 3.328 to 3.628 Å. The geometry around the platinum atom is pseudo square planar with P(1), C(1), P(2), and, presumably, H(2) (see

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(9) Immirzi, A.; Musco, A.; Pregosin, P. S.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 721.

(10) Alcock, N. W.; Howarth, O. S.; Moore, P.; Morris, G. E. *J. Chem. Soc., Chem. Commun.* **1979**, 1160.

(11) Churchill, M. R.; Chang, S. W. Y. *Inorg. Chem.* **1974**, *13*, 2413.

Scheme I) as donor atoms although the hydride ligands could not be located in the X-ray analysis. The geometry around tungsten, as in compound **4**, may be regarded as pseudotetrahedral with the two cyclopentadienyl rings in an almost eclipsed conformation. The plane defined by the centers of gravity of the two rings and the tungsten atom and the plane defined by the platinum and the two phosphorus atoms make a dihedral angle of 93.1°, implying that the two hydride ligands are approximately coplanar with P(1), C(1), and P(2). Compound **3b** contains a single W–H–Pt bridge with its hydrogen atom completing the square-planar coordination around the platinum atom. The second hydride ligand is present as a terminal ligand. This structural assignment can be inferred from the significantly different P–Pt–W bond angles (see Table I) and the corresponding ligand arrangements about the tungsten and platinum centers. Unlike in **4**, the two Cp rings in **3b** are not symmetrically placed relative to the $Pt(Ph)(PEt_3)_2$ fragment, indicating that the two Pt–H separations are markedly different.

A similar, albeit less marked, increase in M–M bond distance, associated with a decrease in number of M–H–M bridging units, has been observed in the case of the two isomeric compounds $[(Et_3P)_2Pt(\mu\text{-}H)_2Pt(Ph)(PEt_3)_2][BPh_4]$ (Pt–Pt = 2.819 (1) Å) and $[(Et_3P)_2(H)Pt(\mu\text{-}H)Pt(Ph)(PEt_3)_2][BPh_4]$ (Pt–Pt = 3.093 (1) Å).[12]

Finally, mention should be made of the Pt–P bond lengths which are longer in **3b** (average value 2.334 (5) Å) than in **4** (2.216 (5) Å) presumably as a result of the addition of another electron-rich phosphine to the platinum center.

The $^{31}P\{^{1}H\}$ NMR spectrum of **3a** shows a multiplet centered at +8.4 ppm. While the phosphorus atoms are strongly coupled to platinum ($^{1}J(^{195}Pt\text{-}^{31}P)$ = 2736 Hz), no coupling to tungsten is observed. The ^{31}P NMR spectrum of **3a**, recorded under "off-resonance" condition, shows the presence of two hydrogen atoms coupled to phosphorus. The ^{1}H NMR spectrum of **3a** in CD_2Cl_2 shows that the two hydride ligands are equivalent on the NMR time scale. At ca. −20 °C they appear as a triplet centered at −18.7 ppm arising from couplings to the two phosphosrus atoms ($^{2}J(^{31}P\text{-}^{1}H)$ = 3.7 Hz). In addition one observes signals associated with the isotopomers ^{183}W and ^{195}Pt ($^{1}J(^{183}W\text{-}^{1}H)$ = 59.7 Hz and $^{1}J(^{195}Pt\text{-}^{1}H)$ = 192.3 Hz). The spectrum is temperature dependent: (1) the multiplet broadens at ca. −40 °C, (2) it coalesces to a single very broad resonance at ca. −80 °C, and (3) no further change is observed on lowering the temperature to ca. −100 °C in THF-d_8. These observations are consistent with the postulate that there are one terminal and one bridging hydride ligand in this compound exchanging rapidly even at the lowest temperature that could be reached.

Another significant difference in NMR parameters between **3** and **4** is the larger value of $^{1}J(^{195}Pt\text{-}^{1}H)$ in **4** (620–720 Hz) than in **3** (192.3 Hz). The latter value could arise as the average of a large value of $^{1}J(^{195}Pt\text{-}^{1}H^{2})$ and a small value of $^{3}J(^{195}Pt\text{-}^{1}H^{1})$ if one assumes that the bridging hydride exchange is fast on the NMR time scale.

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Registry No. 1, 1271-33-6; 2, 85799-24-2; 3a, 85762-70-5; 3b, 85799-25-3; 4, 85762-72-7.

Supplementary Material Available: Tables containing positional and thermal parameters for non-hydrogen atoms (Table S1), bond lengths and angles (Table S2), and observed and calculated structure factors (Table S3) for both structures (51 pages). Ordering information is given on any current masthead page.

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[12] Bachechi, F.; Zambonelli, L.; Venanzi, L. M., unpublished observations. See also: Venanzi, L. M. *Coord. Chem. Rev.* 1982, *43*, 251.

[13] Petersen, J. L.; Masino, A.; Stewart, R. P. *J. Organomet. Chem.* 1981, *203*, 55.

Unexpected Intramolecular Nucleophilic Substitution in an Anionic $Fe_2(CO)_6$ Complex with an Organosulfur Ligand. A Novel Preparation of $Fe_2(CO)_6$ Complexes of Dithioformic Acid Esters

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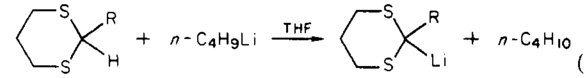
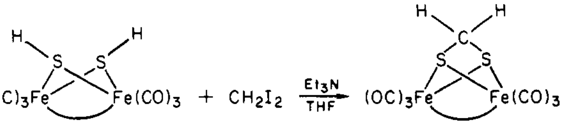
Summary: The carbanion formed by lithium diisopropylamide deprotonation of $(\mu\text{-}CH_2S_2)Fe_2(CO)_6$ undergoes intramolecular nucleophilic attack at iron to give a C–Fe bond and a sulfur-centered anion. Alkylation then forms a bridging alkylthio ligand. The structure of the alkylation product obtained by reaction with $CH_3C(O)CH_2Br$ was determined by X-ray crystallography, as was the structure of an isomer obtained by the piperidine-induced reaction of $(\mu\text{-}HS)_2Fe_2(CO)_6$ with $HC{\equiv}CC(O)CH_3$.

The facile metalation of 1,3-dithianes (eq 1) provides the basis for the very useful nucleophilic acylation method developed by Corey and Seebach.[2] During our initial



(1)

studies of the chemistry of (μ-dithio)bis(tricarbonyliron)[3] we prepared $(\mu\text{-}CH_2S_2)Fe_2(CO)_6$, **1**,[4] by reaction of the $[(\mu\text{-}S)_2Fe(CO)_6]^{2-}$ anion with diiodomethane. In subsequent work, we developed another procedure which produced this compound in higher yield (eq 2).[5] Since it may



1 (2)

be expected that the sulfur atoms in **1** bear a partial positive charge as a consequence of lone-pair donation to iron, an organolithium reagent derived from **1**, i.e., **2**,

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[1] (a) Massachusetts Institute of Technology. (b) University of Alberta. (c) On leave from Nankai University, Tian-Jin, PRC, 1979–1981. (d) Natural Sciences and Engineering Research Council Postdoctoral Fellow.

[2] Corey, E. J.; Seebach, D. *Angew. Chem.* 1965, *77*, 1135. See also: Seebach, D. *Synthesis* 1969, 21.

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