Reaction of 1 with benzonitrile also occurs with elimination of ethylene to produce the 2,5-diazatitanacyclopent-2-ene complex 4 (Scheme I).[14] Compound 4 is sufficiently stable to be isolated. However, over days in solution it was found to isomerize to the 2,5-diazatitanacyclopent-3-ene derivative **5** (Scheme I),[15] which was more readily purified as its pyridine adduct **6**.[16] The kinetic product 4 was subjected to a single-crystal X-ray diffraction analysis.[17] Previous work has shown that 2,5-diazatitanacyclopent-3-ene (ene–diamido) derivatives such as 5 are bent with fold angles close to 50°.[18] In contrast, the metallacyclic ring in 4 is rigorously planar (Figure 1). The coordination environment about titanium is pseudotetrahedral. While the two Ti–N distances of 1.886 (2) and 1.910 (2) Å are comparable to those found in ene–diamido compounds of titanium,[18] the C–N distances of 1.277 (3) and 1.466 (3) Å are consistent with the structure shown for 4 (Scheme I).

Acknowledgment. We thank the National Science Foundation (Grant CHE-8915573) for support of this research.

Supplementary Material Available: Text describing the X-ray diffraction study and tables of crystal data and data collection parameters, positional parameters, general temperature factors, and bond distances and angles for 4 (23 pages). Ordering information is given on any current masthead page.

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(13) High-resolution MS for $CHEtCEtCHPhNHCH_2Ph$: calcd, 280.2062; found, 280.2062. ${}^{1}H$ NMR (C_6D_6, 30 °C; δ): 7.04–7.42 (aromatics); 5.62 (t, C*H*Et); 4.41 (s, C*H*Ph); 3.63 (dd, CH_2Ph); 1.97 (m, C$H_2$$CH_3$); 1.32 (broad, N*H*); 0.94 (t), 0.80 (t, CH_2CH_3). Selected ${}^{13}C$ NMR (C_6D_6, 30 °C; δ): 68.7 (*C*HPh); 52.2 (*C*H_2Ph); 21.6, 21.4 (*C*H_2CH_3); 14.9, 14.5 (CH_2*C*H_3). High-resolution MS for $CHPhCHCHPhNHCH_2Ph$: calcd, 299.1674; found, 299.1668. ${}^{1}H$ NMR (C_6D_6, 30 °C; δ): 7.0–7.45 (aromatics); 6.51 (d, =C*H*Ph); 6.25 (dd, =C*H*); 4.26 (d, NC*H*Ph); 3.65 (s, NCH_2Ph); 1.89 (broad, N*H*). Selected ${}^{13}C$ NMR (C_6D_6, 30 °C; δ): 65.1 (N*C*HPh); 51.8 (N*C*H_2Ph).

(14) Anal. Calcd for $TiC_{63}H_{50}N_2O_2$ ($4{\cdot}C_6H_6$): C, 82.70; H, 5.51; N, 3.06. Found: C, 83.32; H, 5.78; N, 2.99. ${}^{1}H$ NMR (C_6D_6, 30 °C; δ): 6.73–7.62 (aromatics); 5.81 (s, C*H*Ph); 3.72 (d), 2.96 (d, CH_2Ph); 161.4, 160.7 (Ti–O–*C*); 90.6 (*C*HPh); 53.5 (*C*H_2Ph).

(15) (a) Isomerization of a 2-azatitanacyclopent-2-ene ring has been reported; see: Cohen, S. A.; Bercaw, J. E. *Organometallics* **1985**, *4*, 1006. (b) For the isomerization of 2-azametallacyclopentene rings see: Strickler, J. R.; Wigley, D. E. *Organometallics* **1990**, *9*, 1605 and references therein.

(16) ${}^{1}H$ NMR for **5** (C_6D_6, 30 °C; δ): 6.36–7.36 (aromatics); 4.21 (s, CH_2Ph). Selected ${}^{13}C$ NMR for **5** (C_6D_6, 30 °C; δ): 159.2 (Ti–O–*C*); 117.0, 115.0 (TiNH*C*Ph*C*Ph); 58.4 (*C*H_2Ph). Anal. Calcd for $TiC_{62}H_{49}N_3O_2$ (**6**): C, 81.30; H, 5.39; N, 4.59. Found: C, 81.67; H, 5.57; N, 4.49. ${}^{1}H$ NMR for **6** (C_6D_6, 30 °C; δ): 9.91 (broad N*H*); 6.13–7.60 (aromatics); 4.62 (s, CH_2Ph). Selected ${}^{13}C$ NMR for **6** (C_6D_6, 30 °C; δ): 160.6 (Ti–O–*C*); 56.4 (*C*H_2Ph).

(17) X-ray crystal data for $TiC_{63}H_{50}N_2O_2$, ($4{\cdot}C_6H_6$) at −50 °C: a = 10.149 (2) Å, b = 13.738 (2) Å, c = 17.774 (2) Å, α = 94.55 (1)°, β = 101.53 (1)°, γ = 93.66 (1)°, Z = 2, d_{calcd} = 1.260 g cm^{-3} in space group $P\bar{1}$ (No. 2). Of the 6271 unique data collected with Mo Kα radiation ($4° \le 2\theta \le 45°$), the 4728 with $I > 3\sigma(I)$ were used in the final refinements to yield R = 0.035 and R_w = 0.038. Hydrogen atoms were placed in ideal positions and were not refined.

(18) (a) Shur, V. B.; Berkovich, E. G.; Volpin, M. E.; Lorenz, B.; Wahren, M. *J. Organomet. Chem.* **1982**, *228*, C36. (b) Shur, V. B.; Bernadyuk, S. Z.; Burlakov, V. V.; Andrianov, V. G.; Yanovsky, A. I.; Struchkov, Y. T.; Volpin, M. E. *J. Organomet. Chem.* **1983**, *243*, 157.

Articles

Rhenium–Platinum Mixed-Metal Clusters. Synthesis and Solid-State Structural Characterization of $[Re_2Pt(\mu\text{-}H)_2(CO)_8(COD)]$ and of $[Re_3Pt(\mu\text{-}H)_3(CO)_{14}]$

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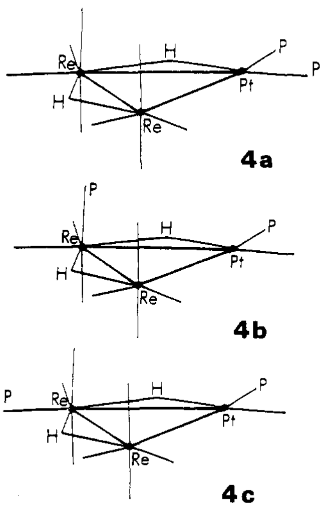
The reaction of $[Re_2(\mu\text{-}H)_2(CO)_8]$ with 1 equiv of $Pt(COD)_2$ (COD = 1,5-cyclooctadiene) affords quantitatively the triangular cluster $[Re_2Pt(\mu\text{-}H)_2(CO)_8(COD)]$, characterized spectroscopically and by X-ray analysis. The crystals are monoclinic, space group $P2_1$, with a = 7.217 (3) Å, b = 17.081 (5) Å, c = 8.577 (3) Å, β = 109.96 (3)°, and Z = 2. The refinements, based on 2037 significant reflections, gave final agreement indices R and R_w of 0.021 and 0.025, respectively. The ligand COD can be easily substituted by two PPh_3 molecules. On the contrary, the reaction with 2 equiv of CO, at 190 K, leads to the substitution of COD by one CO and one $HRe(CO)_5$ molecule, giving the complex $[Re_3Pt(\mu\text{-}H)_3(CO)_{14}]$, whose structure has been elucidated by X-ray analysis. It gives triclinic crystals, space group $P\bar{1}$, with a = 11.764 (1) Å, b = 13.737 (4) Å, c = 15.787 (3) Å, α = 64.83 (2)°, β = 83.36 (1)°, γ = 89.19 (2)°, and Z = 4. The refinements, based on 4461 significant reflections, gave final agreement indices R and R_w of 0.031 and 0.032, respectively. The structure contains a tetrametal cluster consisting of a Re_2Pt triangle plus a Re atom, which belongs to an unusual $HRe(CO)_5$ two-electron donor ligand, bound to the platinum atom. The ${}^{1}H$ NMR spectrum of this complex shows, at 180 K, the presence of two isomers.

We are currently investigating rational approaches to the synthesis of Re–Pt mixed-metal clusters, as potential models or precursors to catalytic species. Following the method developed by the Stone group,[1] trimetallacyclo-

Chart I



propane compounds have been obtained by addition of the ethylene-like molecule $[Re_2(\mu\text{-}H)_2(CO)_8]$ (compound 1) to the carbenoid fragment "$Pt(PPh_3)_2$", originated from $[Pt(PPh_3)_2(C_2H_4)]$.[2] The reaction of the same Pt complex with $[Re_2(CO)_{10}]$ afforded the $[Re_2(PtPPh_3)_n(CO)_{10}]$ clusters (n = 1–3), with structures based on Re_2Pt triangles condensed on the Re–Re hinge.[3] The interest in precursors to catalysts not containing phosphorus atoms prompted us to investigate the reactivity between rhenium carbonyl compounds and the complex $[Pt(COD)_2]$ (compound 2, COD = 1,5-cyclooctadiene). The coordinatively unsaturated Pt(COD) fragment is able to add across a formally unsaturated metal–metal bond, as demonstrated by the reactions of compound 2 with $[Rh_2(\mu\text{-}CO)_2Cp^*{}_2]$ ($Cp^* = C_5Me_5$),[4] $[Rh_2(\mu\text{-}CO)(\mu\text{-}NO)Cp^*{}_2]^+$,[4] $[Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)Cp_2]$ ($Cp = C_5H_5$),[5] or $[Os_3(\mu\text{-}H)_2(CO)_{10}]$.[6] A similar reaction occurs between $[Pt(COD)_2]$ and $[Re_2(\mu\text{-}H)_2(CO)_8]$, affording quantitatively the mixed-metal triangular cluster $[Re_2Pt(\mu\text{-}H)_2(CO)_8(COD)]$, as we have preliminarily communicated.[7] We report here the details of the synthesis and the spectroscopic characterization of the novel compound, as well as its single-crystal X-ray analysis. Some reactivity of the novel cluster is also discussed, including the synthesis, the solid-state X-ray structure, and the characterization in solution of the novel $[Re_3Pt(\mu\text{-}H)_3(CO)_{14}]$ cluster, containing an unusual ligand as $[HRe(CO)_5]$.

Results and Discussion

The treatment of a CH_2Cl_2 solution of $[Re_2(\mu\text{-}H)_2(CO)_8]$ (1), at 253 K, with 1 equiv of $Pt(COD)_2$ (2) results in the instantaneous and quantitative formation of the novel triangular cluster $[Re_2Pt(\mu\text{-}H)_2(CO)_8(COD)]$ (compound 3), as shown by IR and ^1H NMR monitoring. The compound, which can be isolated as a yellow solid by flash chromatography or by precipitation with n-hexane, exhibits two hydride resonances (δ −9.17, $J_{H\text{-}Pt}$ 755 Hz, δ −16.03, $J_{H\text{-}Pt}$ 22 Hz, CD_2Cl_2, 233 K), that compare well with those of the related clusters $[Re_2Pt(\mu\text{-}H)_2(CO)_8(PPh_3)_2]$ (compounds 4, three isomers, Chart I), obtained by reaction of 1 with $[Pt(PPh_3)_2(C_2H_4)]$.[2] The values of $J_{H\text{-}Pt}$ clearly indicate that one H is directly bound to Pt, bridging a Re–Pt interaction, whilst the second one is bridging the Re–Re bond. The reaction, therefore, leads to the insertion of a PtL_2 fragment (L_2 = COD) into a Re(μ-H)Re bond of 1, as observed when L = PPh_3. The value of the $J_{H\text{-}Pt}$ of the Pt-bound hydride is significantly higher than those observed for the corresponding hydride in the three isomers of 4 (502–668 Hz), suggesting a lower trans influence of the olefin with respect to CO and PPh_3.

The IR spectrum of 3 in the ν(CO) region (see Experimental Section) has a pattern identical to that of isomer **4a**, in which both the phosphines are bound to Pt, in agreement with their similar symmetry. The ν(CO) frequencies of 3 are shifted to higher values (5–10 cm^{-1}) with respect to **4a**, indicating that the $Pt(PPh_3)_2$ fragment provides an higher electron density than the Pt(COD) one, and therefore that the two PPh_3 ligands are better σ-donors and/or poorer π-acceptors than the diene.

A single-crystal X-ray analysis (see below) has confirmed in the solid state the structure suggested from the spectroscopic data in solution.

The ^1H NMR spectrum shows the occurrence in solution of some fluxional process, since, even at 183 K, there are only two resonances due to the COD ligand (intensity 4:8), instead of the expected four. Also in the ^{13}C NMR spectrum at 263 K the CH and CH_2 groups each give rise to only one signal. The carbonyls' spectrum consists of three signals, with intensity ratio 2:1:1, confirming an apparent C_{2v} symmetry in solution.

Three types of dynamic processes, that increase the apparent symmetry in related M_2Pt triangular clusters, have been reported: (a) the rotation of the whole Pt(H)LL′ moiety, as observed in $[Rh_2Pt(\mu\text{-}CO)_2(\mu\text{-}H)(L)(L')Cp^*{}_2]^+$ (L, L′ = COD; L, L′ = CO; L = CO, L′ = PPh_3);[8] (b) the rotation of the COD ligand itself, as observed in $[Rh_2Pt(\mu\text{-}CO)(\mu\text{-}NO)(COD)Cp^*{}_2]^+$;[4] (c) the jump of the hydride between the two Pt–M edges, as observed in **4a**.[9] The ^1H and ^{13}C NMR data of the COD ligand in compound 3 cannot be accounted for by process a, while the symmetry of the carbonyls cannot arise from process b. When the temperature is lowered, in the ^{13}C NMR spectrum it is observed the simultaneous broadening of the carbonyls' and COD resonances (and eventually, at ca. 185 K, the signals of the CH groups and of the highest field carbonyls are almost collapsed). This suggests the occurrence of a single dynamic process, namely the jump of the hydride between the two Pt–Re edges. In the family of mixed Re_2Pt triangular clusters, this process appears therefore to require a lower energy than the rotation of the whole Pt(H)LL′ moiety, formally a d^9 ML_3 fragment,[10] observed in Rh_2Pt triangular clusters.[8]

Compound 3 not only fulfills the requirements for a suitable Re–Pt catalyst precursor but also is a versatile

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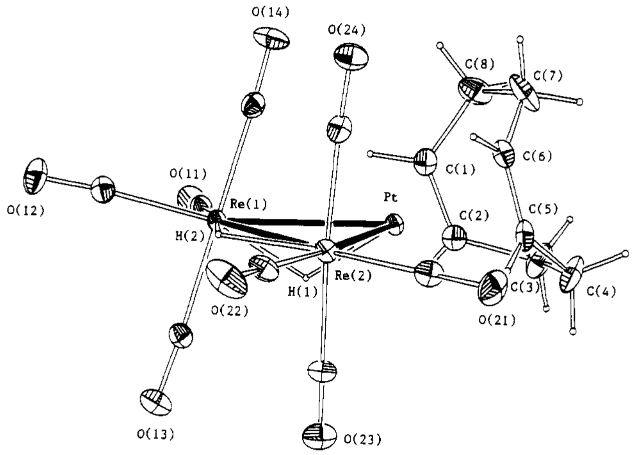

Figure 1. ORTEP drawing of $[Re_2Pt(\mu\text{-}H)_2(CO)_8(COD)]$ (**3**). The carbonyl ligands are indicated by the labels of the oxygen atoms.

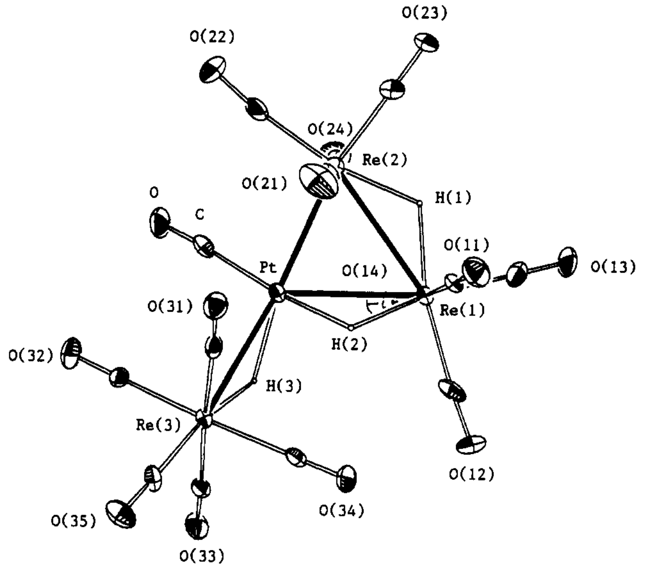

Figure 2. ORTEP drawing of $[Re_3Pt(\mu\text{-}H)_3(CO)_{14}]$ (**5**), molecule A. The carbonyl ligands are indicated by the labels of the oxygen atoms.

intermediate for the synthesis of a variety of derivatives, due to the presence of the labile diene bound to Pt. Treatment of **3** with 2 equiv of PPh_3 at 253 K immediately leads to displacement of the diene, with quantitative formation of compound **4a**, which at higher temperature irreversibly rearranges to the equilibrium mixture of the other two isomers of **4**, as already observed.[2]

The reaction of **3** with CO is completely different. We have not been able to obtain the derivative corresponding to the substitution of the diene by two CO molecules, even if many attempts were made in different experimental conditions. On bubbling CO at room temperature in a solution of **3**, a mixture of species was obtained, the main component being (on the basis of IR monitoring) the complex $[Re_2Pt(CO)_{12}]$, containing two $Re(CO)_5$ groups bound to a *trans*-$Pt(CO)_2$ moiety.[11] In these conditions, therefore, CO is able to displace not only the diene, but also the hydrides, breaking the Re–Re bond. The formation of some black precipitate (likely Pt or $[Pt(CO)_2]_n$ oligomers) and of a little amount of $[Re_2(CO)_{10}]$ is also observed, indicating decomposition of the mixed-metal moiety.

The reaction was then repeated at low temperature (193 K) and with 2 equiv of CO. ^1H NMR monitoring showed the occurrence of a fast reaction, leading mainly to the formation of a novel species, exhibiting at 180 K three hydride resonances of equal intensity, at δ −5.44 ($J_{H\text{-}Pt}$ 632 Hz), −8.57 ($J_{H\text{-}Pt}$ 489 Hz), and −15.70 ($J_{H\text{-}Pt}$ 38 Hz). This species has been identified by a single-crystal X-ray analysis as the complex $[Re_3Pt(\mu\text{-}H)_3(CO)_{14}]$ (compound **5**), which can be considered derived from **3**, by replacement of the diene by one CO and one $[HRe(CO)_5]$ molecule (see below, Figure 2).

The formation of $[HRe(CO)_5]$ derives likely from the decomposition of some starting **3** (compound **1** itself is able to react with CO to give $[HRe(CO)_5]$). A possible overall stoichiometry of the reaction is

$$3[Re_2Pt(\mu\text{-}H)_2(CO)_8(COD)] + 6CO \rightarrow 2[Re_3Pt(\mu\text{-}H)_3(CO)_{14}] + \text{“}Pt(CO)_2\text{”} + 3COD$$

It is surprising that the expected derivative of displacement of the diene by two CO molecules was not obtained. However, the triangular clusters M_2Pt containing two CO bound to Pt described in the literature[10] have been obtained by routes different from the displacement of the diene, even when the corresponding COD derivatives were available. In particular, in the Rh systems investigated by Stone's group, the reaction of the unsaturated dimer $[Rh_2(\mu\text{-}CO)_2Cp^*_2]$ with $[Pt(COD)_2]$ gave the triangular cluster $[Rh_2Pt(\mu\text{-}CO)_2(COD)Cp^*_2]$, analogous to **3**, but the derivative with two CO bound to Pt was synthesized by reaction of $[Pt(COD)_2]$ with 2 equiv of the mononuclear complex $[Rh(CO)_2Cp^*]$.[4b] In the present case the direct reaction between $[Pt(COD)_2]$ and $[HRe(CO)_5]$ (even in the ratio 1:2) affords again compound **5**.

$$[Pt(COD)_2] + 3[HRe(CO)_5] \rightarrow [Re_3Pt(\mu\text{-}H)_3(CO)_{14}] + CO + COD$$

Better yields of **5** are obtained by treating **3** with 1 equiv of $[HRe(CO)_5]$ and ca. 1 equiv of CO. The use of 2 equiv of $[HRe(CO)_5]$, without CO, gives again **5** as the main reaction product: it is not possible therefore to replace the diene by two $[HRe(CO)_5]$ ligands.

The three main resonances observed in the hydride region of the ^1H NMR spectrum are in line, both for chemical shifts and couplings, with that expected on the basis of the solid-state structure for two hydrogens bridging Pt and Re (−5.44 and −8.57 ppm) and one hydrogen bridging two Re atoms (−15.70 ppm). The spectra at 180 K of samples of **5**, purified by flash chromatography, always show, besides the above mentioned resonances, the presence of another set of three resonances at δ −6.16 ($J_{H\text{-}Pt}$ 736 Hz), −9.47 ($J_{H\text{-}Pt}$ 672 Hz), and −16.37 ($J_{H\text{-}Pt}$ <20 Hz) with a relative ratio 1:1:1 and with an integrated intensity ratio of ca. 1:19 with respect to the other ones (Figure 3). The presence of these resonances is detectable only at temperatures lower than 195 K, and their line width decreases significantly with the temperature. The values of the chemical shifts and couplings of these resonances and their variable-temperature behavior suggest that this minor species is an isomer of compound **5**, with two hydrides bridging Pt–Re edges and one bridging a Re–Re one. The differences in the structure of the two isomers (**5a**, **5b**) and their dynamic behavior are currently under investigation and will be reported in a separate paper.

The chemical shift of the Pt atom of compounds **3** and **5a** have been determined by means of a 2D ^1H–^{195}Pt correlation experiment performed in the "reverse mode" [δ 1424 at 263 K for compound **3** and δ 718 at 186 K for compound **5a** (Figure 4), respectively]. The ^{195}Pt chemical

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(11) Urbancic, M. A.; Wilson, S. R.; Shapley, J. R. *Inorg. Chem.* **1984**, *23*, 2954.

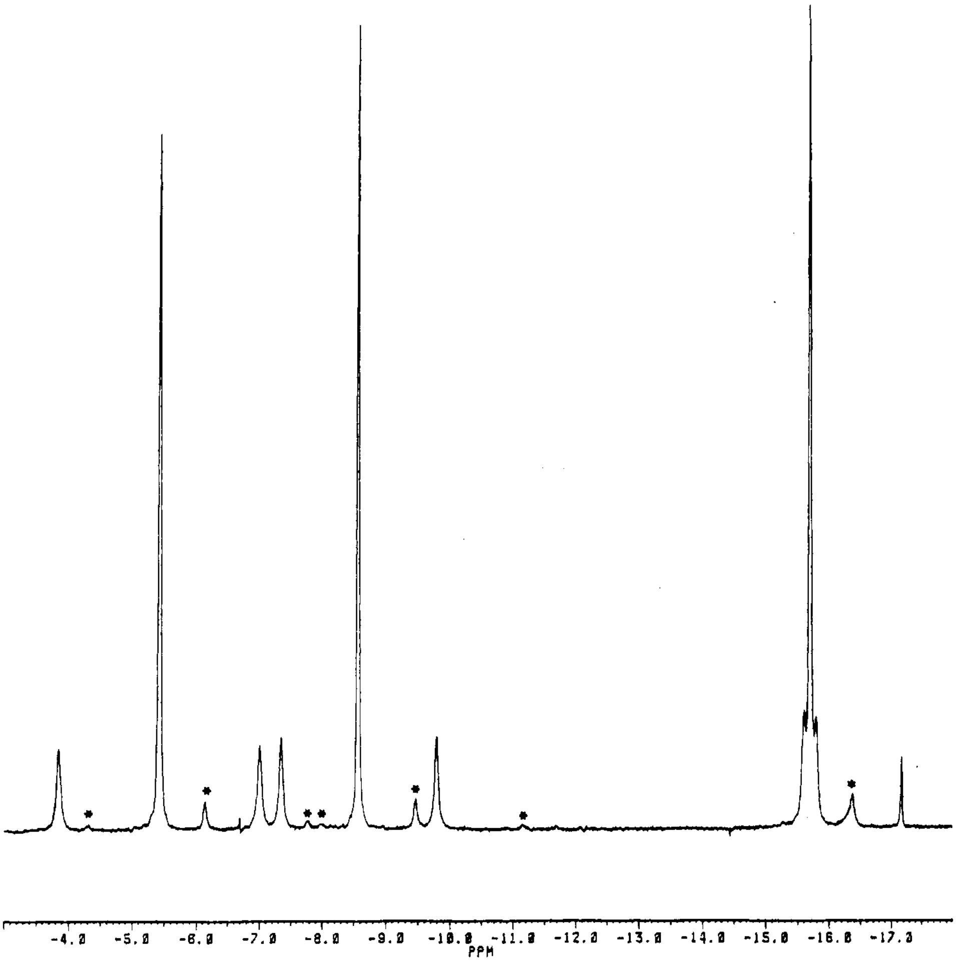

Figure 3. Hydride region of the ^{1}H spectrum of compound **5** (200 MHz, 180 K, CD_2Cl_2). The resonances of the minor isomer **5b** are indicated by asterisks. The resonance at −17.2 ppm is due to an impurity of $[Re_3(\mu\text{-}H)_3(CO)_{12}]$.

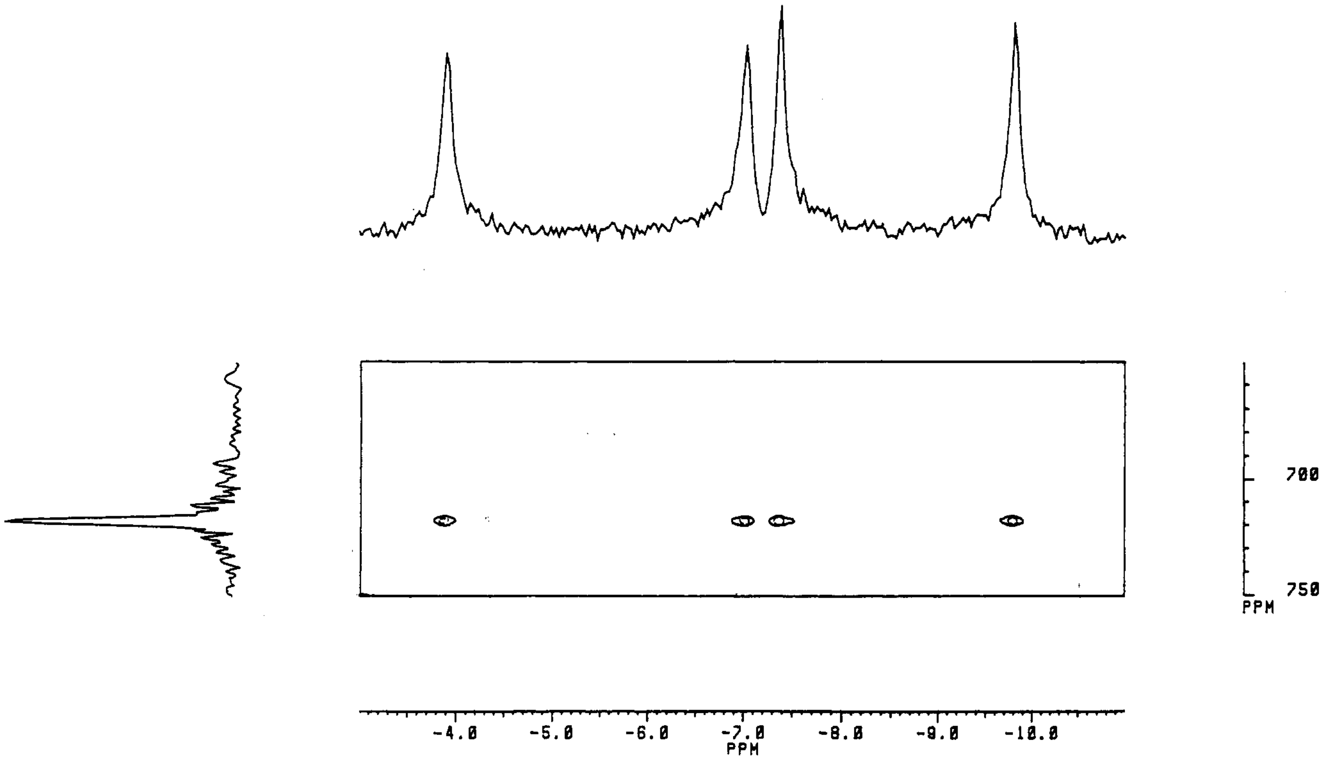

Figure 4. ^{1}H–^{195}Pt 2D reverse-correlation experiment of compound **5a** (186 K, CD_2Cl_2). A total of 48 FIDs of 1K data points were recorded for each of the 128 increments of t_1 (spectral width in F_2 3000 Hz; spectral width in F_1 16 000 Hz; relaxation delay 0.6 s). The data matrix was zero-filled twice in the F_1 dimension before transformation without any weighting functions. Both F_2 and F_1 projections are shown in the figure.

Table I. Bond Distances (Å) and Angles (deg) for [$Re_2Pt(\mu\text{-}H)_2(CO)_8(COD)$] (3)

	Distances		
Pt–Re1	2.895 (1)	Re2–C22	1.93 (2)
Pt–Re2	2.741 (1)	Re2–C23	2.01 (1)
Re1–Re2	3.115 (1)	Re2–C24	1.97 (2)
Pt–C1	2.31 (1)	C1–C2	1.38 (2)
Pt–C2	2.34 (1)	C2–C3	1.48 (2)
Pt–C5	2.18 (1)	C3–C4	1.46 (2)
Pt–C6	2.20 (1)	C4–C5	1.52 (2)
Re1–C11	1.93 (1)	C5–C6	1.39 (2)
Re1–C12	1.95 (2)	C6–C7	1.45 (2)
Re1–C13	1.96 (1)	C7–C8	1.51 (3)
Re1–C14	2.00 (2)	C8–C1	1.49 (2)
Re2–C21	1.90 (2)	C–O	1.11 (2)–1.17 (2)
	Angles		
Re1–Pt–Re2	67.03 (2)	Re2–Re1–C14	87.1 (4)
Pt–Re1–Re2	54.12 (1)	Pt–Re2–C21	98.0 (4)
Pt–Re2–Re1	58.84 (1)	Pt–Re2–C22	173.7 (5)
Pt–Re1–C11	99.9 (5)	Pt–Re2–C23	84.3 (3)
Pt–Re1–C12	160.7 (4)	Pt–Re2–C24	86.5 (4)
Pt–Re1–C13	106.4 (4)	Re1–Re2–C21	156.4 (4)
Pt–Re1–C14	73.8 (4)	Re1–Re2–C22	114.9 (5)
Re2–Re1–C11	153.9 (5)	Re1–Re2–C23	84.0 (4)
Re2–Re1–C12	114.4 (4)	Re1–Re2–C24	91.5 (4)
Re2–Re1–C13	93.7 (4)	Re–C–O	175 (1)–180 (1)

shifts are extremely sensitive to small changes in the environment, and their trend is not easily predictable.[10,12] However, we can observe that in [M_2PtLL'] compounds ^{195}Pt becomes more shielded on passing from L, L′ = COD to L = CO, L′ = PPh_3 both when M_2 is $Re_2H_2(CO)_8$, as in compounds **3** and **4b** or **4c** (δ 282 and 196),[2] and when M_2 is [$Rh_2(\mu\text{-}CO)_2Cp^*{}_2$], as in [$Rh_2Pt(\mu\text{-}CO)_2(COD)Cp^*{}_2$] and [$Rh_2Pt(\mu\text{-}CO)_2(CO)(PPh_3)Cp^*{}_2$],[4b] where δ 934 and −5.8,[10] respectively. The chemical shift of ^{195}Pt in compound **5a** is intermediate between the two, but no simple correlation with the electronic properties of the ligands can be suggested.

Description of the Structures of Compounds 3 and 5. Both crystal structures consist of the packing of discrete molecules of the complexes, separated by normal van der Waals contacts. In the case of compound **5** there are two crystallographically independent molecules (A and B) per asymmetric unit.

The molecular structures of [$Re_2Pt(\mu\text{-}H)_2(CO)_8(COD)$] (**3**) and [$Re_3Pt(\mu\text{-}H)_3(CO)_{14}$] (**5**) are illustrated in Figures 1 and 2, and bond distances and angles are reported in Tables I and II, respectively.

Compound **3** contains an irregular triangular Re_2Pt cluster, with two significantly different Pt–Re edges. Each Re atom bears four terminal CO ligands, and the Pt atom is π-bonded by the two double bonds of the COD ligand. The structure of compound **5** is related to that of compound **3**, showing the presence of a very similar triangular Re_2Pt moiety, with the Pt atom bearing, instead of the COD ligand, one CO ligand and a [$HRe(CO)_5$] molecule, acting formally as a two-electron donor ligand. The positions of the hydride ligands in both compounds were calculated by use of the program HYDEX.[13] In the triangular moiety one hydride lies in a bridging position on the Re–Re edge, almost coplanar with the metallic triangle, and a second one bridges the longer Pt–Re bond and is well displaced (0.9–1.0 Å) out of the Re_2Pt plane. The rhenium atoms exhibit slightly distorted octahedral coordination geometries, while the platinum atom shows a square-planar environment.

Table II. Bond Distances (Å) and Angles (deg) for [$Re_3Pt(\mu\text{-}H)_3(CO)_{14}$] (5) in the Two Independent Molecules (A and B)

	molecule A	molecule B
	Distances	
Pt–Re1	2.934 (1)	2.938 (1)
Pt–Re2	2.776 (1)	2.769 (1)
Pt–Re3	3.067 (1)	3.050 (1)
Re1–Re2	3.152 (1)	3.145 (1)
Pt–C	1.88 (2)	1.83 (2)
Re1–C11	2.00 (2)	1.98 (2)
Re1–C12	1.96 (2)	1.93 (2)
Re1–C13	1.98 (2)	1.96 (2)
Re1–C14	2.01 (2)	2.02 (2)
Re2–C21	1.97 (3)	1.97 (3)
Re2–C22	1.93 (2)	1.98 (2)
Re2–C23	1.90 (2)	1.89 (2)
Re2–C24	1.97 (2)	2.00 (2)
Re3–C31	1.98 (2)	2.04 (2)
Re3–C32	1.98 (2)	2.01 (2)
Re3–C33	2.02 (2)	2.00 (2)
Re3–C34	2.05 (2)	2.03 (2)
Re3–C35	1.92 (2)	1.97 (2)
C–O	1.10 (2)–1.17 (2)	1.10 (2)–1.16 (2)
	Angles	
Re1–Pt–Re2	66.94 (2)	66.80 (2)
Re1–Pt–Re3	116.88 (3)	120.39 (2)
Re2–Pt–Re3	158.01 (3)	157.42 (3)
Pt–Re1–Re2	54.12 (2)	54.03 (2)
Pt–Re2–Re1	58.94 (2)	59.17 (2)
Re1–Pt–C	142.4 (5)	143.2 (5)
Re2–Pt–C	82.6 (5)	82.5 (5)
Re3–Pt–C	99.7 (5)	95.7 (5)
Pt–Re1–C11	104.6 (5)	103.4 (5)
Pt–Re1–C12	106.8 (5)	106.6 (5)
Pt–Re1–C13	158.1 (5)	158.0 (5)
Pt–Re1–C14	73.3 (5)	74.2 (5)
Re2–Re1–C11	92.6 (5)	90.2 (5)
Re2–Re1–C12	160.9 (5)	160.0 (5)
Re2–Re1–C13	110.7 (5)	111.5 (5)
Re2–Re1–C14	83.9 (4)	86.0 (4)
Pt–Re2–C21	80.2 (7)	80.3 (5)
Pt–Re2–C22	102.0 (5)	101.3 (4)
Pt–Re2–C23	165.7 (6)	168.3 (5)
Pt–Re2–C24	94.5 (5)	93.3 (4)
Re1–Re2–C21	86.2 (7)	86.2 (4)
Re1–Re2–C22	160.9 (5)	160.4 (4)
Re1–Re2–C23	108.3 (5)	110.9 (4)
Re1–Re2–C24	93.1 (5)	91.3 (5)
Pt–Re3–C31	67.7 (4)	67.6 (4)
Pt–Re3–C32	87.5 (5)	87.6 (5)
Pt–Re3–C33	109.1 (4)	112.6 (5)
Pt–Re3–C34	89.5 (4)	87.3 (4)
Pt–Re3–C35	160.5 (5)	157.8 (5)
Pt–C–O	175 (2)	176 (2)
Re–C–O	172 (2)–180 (1)	173 (2)–179 (1)

These species can be considered as belonging to the family [$Re_2Pt(\mu\text{-}H)_2(CO)_8LL'$] (L and L′ = two-electron donor ligand); the family also includes the already reported [$Re_2Pt(\mu\text{-}H)_2(CO)_8(PPh_3)_2$] (isomer **4b**),[2] with one PPh_3 ligand axially bound on a Re atom and with the Pt atom bearing one CO group and the second PPh_3 ligand. The bond parameters common to the three members of the family show similar values. The hydrogen-bridged Re1–Re2 edge slightly increases from 3.115 (1) Å in **3** to 3.152 (1) and 3.145 (1) Å in the two molecules of **5** to 3.203 (1) Å in **4b**. The more marked lengthening found in **4b** is very likely due to the presence of the axial PPh_3 on Re1. The two Pt–Re edges within each triangle are significantly different (0.12–0.17 Å). The hydrogen-bridged Pt–Re1 edge is 2.895 (1) Å in **3**, 2.934 (1) and 2.938 (1) Å in **5**, and 2.906 (1) Å in **4b**. The Pt–Re2 unbridged edge shows values of 2.741 (1) Å in **3**, 2.776 (1) and 2.769 (1) Å in **5**, and 2.788 (1) Å in **4b**.

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In the distorted square-planar coordination geometries at the Pt atoms observed in compounds **3**, **4b**, and **5**, two of the four interactions involve the Re2 atom and the hydride ligand bridging the Pt—Re1 edge. In **3** the two π-bonds with the COD molecule complete the coordination sphere. These two bonds are significantly different: that lying trans with respect to the Pt—Re2 bond (mean Pt—C distance 2.32 Å, Pt—C* 2.23 Å, Re2—Pt—C* 176°, C* indicating the midpoint of the relevant C═C double bond) is longer than the other one, which is trans to the hydride on the Pt—Re1 edge (mean Pt—C distance 2.19 Å, Pt—C* 2.08 Å, H—Pt—C* 163°). This difference, not observed in compounds without hydrides bridging the M—Pt edges, like $[Fe_2Pt(CO)_8(COD)]$[14] and $[Co_2Pt(CO)_7(COD)]$,[15] seems not due to intramolecular nonbonding repulsions involving the bridging hydride and the COD atoms. It is in line with a greater trans influence of a M—M(M′) bond compared to that of a M(μ-H)M(M′) interaction, as previously observed from the structural data[16] of $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$ and from the NMR parameters ($J_{P—Pt}$) of compound **4a**.[2]

In compound **5** the square-planar coordination of Pt is completed by a CO ligand and a $[HRe(CO)_5]$ molecule bound in approximate trans position with respect to the Pt–Re2 bond [Re2–Pt–Re3 158.01 (3)° in molecule A and 157.42 (3)° in molecule B]. However, the Re3 atom is significantly displaced out of the triangular plane (ca. 1.1 Å), while the bridging hydride H3 is closer to it (displacement of ca. 0.3 Å, mean Re2–Pt–H3 167.1°). The square-planar coordination is therefore more properly defined by the Re2, C, H2, and H3 atoms. On average, the best plane passing through Pt and these four atoms forms a dihedral angle of ca. 25° with the Re_2Pt plane.

The same $[HRe(CO)_5]$ unit was previously observed only in the L-shaped complexes $[Re_3(\mu\text{-}H)(CO)_{14}]$,[17] $[MnRe_2(\mu\text{-}H)(CO)_{14}]$,[18] and $[Mn_2Re(\mu\text{-}H)(CO)_{14}]$,[19] in which it can be viewed as replacing an equatorial CO ligand of the corresponding dinuclear $M_2(CO)_{10}$ species. We can therefore formally consider it as a neutral two-electron donor ligand (while related "ligands", like $[Re(CO)_5]^-$ or $[H_2Re(CO)_4]^-$, are better regarded as pseudo-halides), strong enough to displace an η^1-aldehyde[19] or an alkene. Compound **5** is the first example in which $[HRe(CO)_5]$ is coordinated to a square-planar center.

The Pt–Re3 hydrogen-bridged edge, 3.067 (1) and 3.050 (1) Å in the two independent molecules, is, on average, 0.12 Å longer than the Pt–Re1 hydrogen-bridged interaction and 0.29 Å longer than the Pt–Re2 unbridged edge. An even more pronounced lengthening of the M–Re distance was observed in the aforementioned species containing $[HRe(CO)_5]$ bound to octahedral metal centers.[17-19]

The coordination mode of the $[HRe(CO)_5]$ molecule is such that its equatorial carbonyls are eclipsed with respect to the ligands on Pt, in contrast with the staggered disposition of the $Re(CO)_5$ units with respect to the $Pt(CO)_2$ moiety in $[PtRe_2(CO)_{12}]$. The difference can be ascribed to the presence of the hydride in **5**; however, analogous eclipsed conformations are observed in $[MnRe_2(\mu\text{-}H)(CO)_{14}]$ and $[Mn_2Re(\mu\text{-}H)(CO)_{14}]$, but not in $[Re_3(\mu\text{-}H)(CO)_{14}]$.

Table III. Crystal Data for Compounds 3 and 5

	3	5
formula	$C_{16}H_{14}O_8PtRe_2$	$C_{14}H_3O_{14}PtRe_3$
fw	901.8	1148.9
cryst sys	monoclinic	triclinic
space group	$P2_1$ (No. 4)	$P\bar{1}$ (No. 2)
a, Å	7.217 (3)	11.764 (1)
b, Å	17.081 (5)	13.737 (4)
c, Å	8.577 (3)	15.787 (3)
α, deg	90.00	64.83 (2)
β, deg	109.96 (3)	83.86 (1)
γ, deg	90.00	89.19 (2)
V, Å^3	994 (1)	2292 (1)
Z	2	4
D_c, g cm^{-3}	3.013	3.330
$F(000)$	804	2008
radn (graphite monochr)	Mo Kα	Mo Kα
μ (Mo Kα), cm^{-1}	194.5	222.3
2θ range, deg	6–56	6–50
scan method	ω	ω
scan interval, deg	2.0	1.0
coll octants	$\pm h,+k,+l$	$h,\pm k,\pm l$
no. of data coll (room temp)	2471	7998
no. of data used ($I > 3\sigma(I)$)	2037	4461
no. of variable params	243	289
cryst decay, %	0	0
no. of azimut refl for abs corr	3	3
max–min trans factor	1.00–0.42	1.00–0.80
cryst size, mm	0.12 × 0.15 × 0.23	0.08 × 0.11 × 0.24
weighting "fudge" p factor	0.035	0.030
ESD[a]	1.038	1.142
R[b]	0.021	0.031
R_w[c]	0.025	0.032

[a] $ESD = [\sum w(F_o - kF_c)^2/(N_{obs} - N_{var})]^{1/2}$; $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma(F_o^2) = [\sigma^2(I) + (pI)^2]^{1/2}/Lp$. [b] $R = \sum|F_o - kF_c|/\sum F_o$. [c] $R_w = [\sum w(F_o - kF_c)^2/\sum wF_o^2]^{1/2}$.

Experimental Section

The reactions were performed under N_2, in solvents deoxygenated and dried by standard methods. The IR spectra were recorded in 0.1-mm CaF_2 cells on a Perkin-Elmer 781 grating spectrophotometer, equipped with a data station that uses PE780 software. $[Re_2(\mu\text{-}H)_2(CO)_8]$ and $[Pt(1,5\text{-}C_8H_{12})_2]$ were prepared by literature methods.[20,21]

Synthesis of $[Re_2Pt(\mu\text{-}H)_2(CO)_8(1,5\text{-}C_8H_{12})]$. A sample (26 mg, 0.043 mmol) of $[Re_2(\mu\text{-}H)_2(CO)_8]$ dissolved in CH_2Cl_2 (3 mL) was treated, at 253 K, with $[Pt(1,5\text{-}C_8H_{12})_2]$ (18 mg, 0.044 mmol). The color of the solution turned immediately from yellow to orange, and IR spectra showed the quantitative formation of $[Re_2Pt(\mu\text{-}H)_2(CO)_8(1,5\text{-}C_8H_{12})]$: ν(CO) (CH_2Cl_2) 2096 (s), 2057 (s), 2033 (sh), 2000 (vs), 1962 (vs), 1918 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, 233 K): δ 5.62 ($J_{H\text{-}Pt}$ = 55 Hz, 4 H, CH), 2.01 (8 H, CH_2), −9.17 ($J_{H\text{-}Pt}$ = 755 Hz, 1 H, ReH), −16.03 ($J_{H\text{-}Pt}$ = 22 Hz, 1 H, ReH). ^{13}C NMR (CD_2Cl_2, 263 K): δ 191.0 (4 C, CO), 189.0 (2 C, CO), 186.0 (2 C, CO), 100.1 ($J_{C\text{-}Pt}$ = 80 Hz, 4 C, CH), 31.3 (4 C, CH_2). The solution was concentrated under reduced pressure, at 253 K, and the addition of *n*-hexane caused the formation of a yellow precipitate (29 mg, 0.032 mmol, 74% isolated yield). The product can be isolated also by flash chromatography on a silica gel column (2.5 × 1.5 cm; hexane–CH_2Cl_2 1:1.5). Anal. Calcd for $C_{16}H_{14}O_8PtRe_2$: C, 21.3; H, 1.22. Found: C, 21.0; H, 1.1.

Synthesis of $[Re_3Pt(\mu\text{-}H)_3(CO)_{14}]$. A sample (97 mg, 0.16 mmol) of $[Re_2(\mu\text{-}H)_2(CO)_8]$ dissolved in CH_2Cl_2 (10 mL) was treated, at 253 K, with $[Pt(1,5\text{-}C_8H_{12})_2]$ (67 mg, 0.16 mmol) and then with $[HRe(CO)_5]$ (30 μL, ca. 0.18 mmol) and 4 mL (ca. 0.16 mmol) of CO. IR monitoring showed the formation of $[Re_3Pt(\mu\text{-}H)_3(CO)_{14}]$: ν(CO) (CH_2Cl_2) 2140 (m), 2105 (m), 2086 (sh), 2076 (s), 2030 (vs), 2010 (vs), 1979 (s), 1938 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 180 K): δ −5.44 ($J_{H\text{-}Pt}$ = 632 Hz, 1 H, ReH), −8.57 ($J_{H\text{-}Pt}$ = 489 Hz, 1 H, ReH), −15.70 ($J_{H\text{-}Pt}$ = 38 Hz, 1 H, ReH). The solution was concentrated under reduced pressure, and the addition of *n*-hexane caused the formation of a yellow precipitate of $[Re_3Pt(\mu\text{-}H)_3(CO)_{14}]$ (103 mg, 0.09 mmol, 56% isolated yields).

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Table IV. Final Atomic Fractional Coordinates for $[Re_2Pt(\mu\text{-}H)_2(CO)_8(COD)]$ (3)

atom	*x*	*y*	*z*
Pt	−0.23695 (6)	0.000	−0.18261 (4)
Re1	−0.42019 (6)	−0.15294 (3)	−0.24703 (5)
Re2	−0.17302 (6)	−0.08661 (3)	0.10001 (5)
O11	−0.584 (2)	−0.1492 (8)	−0.629 (1)
O12	−0.675 (2)	−0.2959 (7)	−0.244 (1)
O13	−0.097 (1)	−0.2731 (7)	−0.256 (1)
O14	−0.755 (1)	−0.0378 (7)	−0.250 (1)
O21	0.105 (2)	0.0269 (8)	0.346 (1)
O22	−0.128 (2)	−0.1962 (7)	0.398 (1)
O23	0.181 (1)	−0.1541 (7)	0.014 (1)
O24	−0.535 (1)	0.0007 (7)	0.138 (1)
C11	−0.526 (2)	−0.1505 (9)	−0.486 (1)
C12	−0.586 (2)	−0.2420 (9)	−0.240 (1)
C13	−0.214 (2)	−0.2268 (8)	−0.252 (1)
C14	−0.632 (2)	−0.0777 (9)	−0.245 (1)
C21	−0.000 (2)	−0.0160 (9)	0.253 (1)
C22	−0.146 (2)	−0.1561 (9)	0.283 (1)
C23	0.057 (2)	−0.1301 (8)	0.047 (1)
C24	−0.406 (2)	−0.0332 (9)	0.121 (1)
C1	−0.404 (2)	0.0676 (8)	−0.423 (1)
C2	−0.210 (2)	0.0646 (8)	−0.415 (1)
C3	−0.069 (2)	0.130 (1)	−0.358 (2)
C4	0.031 (2)	0.140 (1)	−0.180 (2)
C5	−0.069 (2)	0.1037 (8)	−0.069 (2)
C6	−0.262 (2)	0.1155 (8)	−0.077 (1)
C7	−0.402 (3)	0.166 (1)	−0.196 (2)
C8	−0.497 (2)	0.135 (1)	−0.370 (2)

Anal. Calcd for $C_{14}H_3O_{14}PtRe_3$: C, 14.6; H, 0.26. Found: C, 15.0; H, 0.22.

NMR Measurements. The NMR spectra were performed on Bruker WP80 and AC200 spectrometers. The 2D heteronuclear correlation experiments have been performed in the reverse mode using a B-SV3 unit as a source of the pulses at the Pt frequency (90° = 28 μs). The pulse sequence used is the one proposed by Bax,[22] in which the correlation is established through the creation of zero and double quantum coherences. Typically, 1K data points were acquired in F_2, while the increments in t_1 were 64 and 128 with repetition delays of 1 and 0.6 s for compounds **3** and **5a**, respectively. The accuracy of ^{195}Pt chemical shifts is better than 1 ppm. The reported δ values are downfield positive with respect to $\Xi(^{195}Pt)$ = 21.400 MHz.

X-ray Analysis. Intensity Measurements. Crystal data are reported in Table III. Both crystal samples were mounted on glass fibers in the air. Data were collected on an Enraf-Nonius CAD4 automated diffractometer using graphite-monochromatized Mo Kα radiation (λ 0.71073 Å). In both cases the setting angles of 25 random intense reflections (16° < 2θ < 25°) were used to determine by least-squares fit accurate cell constants and orientation matrices. The collections were performed by the ω-scan method, using variable scan ranges with a 25% extension at each end of the scan range for background determination. Three standard intense reflections, monitored at regular intervals, were used to check the sample decay during the collections. The intensities were corrected for Lorentz and polarization effects. An empirical absorption correction was applied to the data, based on ψ-scans (ψ 0–360° every 10°) of suitable reflections with χ values close to 90°.

Structure Solutions and Refinements. All computations were performed on a PDP 11/73 computer, using the Enraf-Nonius Structure Determination Package (SDP) and the physical constants tabulated therein.

Table V. Final Atomic Fractional Coordinates for $[Re_3Pt(\mu\text{-}H)_3(CO)_{14}]$ (5)

atom	*x*	*y*	*z*
PtA	0.27238 (5)	0.28831 (5)	0.21364 (4)
Re1A	0.17557 (5)	0.19799 (5)	0.41274 (4)
Re2A	0.03736 (5)	0.24808 (6)	0.24022 (4)
Re3A	0.52735 (5)	0.25515 (5)	0.17148 (4)
OA	0.229 (1)	0.449 (1)	0.0204 (8)
O11A	0.146 (1)	−0.049 (1)	0.4802 (9)
O12A	0.374 (1)	0.168 (1)	0.5332 (8)
O13A	0.013 (1)	0.175 (1)	0.5881 (7)
O14A	0.177 (1)	0.4472 (9)	0.3440 (8)
O21A	0.116 (1)	0.035 (1)	0.240 (1)
O22A	−0.027 (1)	0.324 (1)	0.0377 (8)
O23A	−0.208 (1)	0.162 (1)	0.3156 (9)
O24A	−0.026 (1)	0.478 (1)	0.221 (1)
O31A	0.375 (1)	0.0807 (9)	0.1549 (7)
O32A	0.508 (1)	0.4100 (9)	−0.0379 (7)
O33A	0.675 (1)	0.4300 (9)	0.1919 (7)
O34A	0.533 (1)	0.101 (1)	0.3869 (7)
O35A	0.747 (1)	0.1645 (9)	0.1100 (8)
CA	0.242 (1)	0.385 (1)	0.092 (1)
C11A	0.164 (1)	0.039 (2)	0.452 (1)
C12A	0.304 (1)	0.181 (1)	0.486 (1)
C13A	0.072 (2)	0.183 (2)	0.526 (1)
C14A	0.182 (1)	0.359 (1)	0.367 (1)
C21A	0.091 (2)	0.110 (2)	0.243 (1)
C22A	0.003 (2)	0.296 (2)	0.113 (1)
C23A	−0.116 (1)	0.194 (2)	0.288 (1)
C24A	−0.001 (1)	0.393 (1)	0.229 (1)
C31A	0.428 (1)	0.145 (1)	0.1638 (9)
C32A	0.516 (1)	0.354 (1)	0.038 (1)
C33A	0.621 (1)	0.367 (1)	0.1864 (9)
C34A	0.531 (1)	0.155 (1)	0.311 (1)
C35A	0.665 (1)	0.199 (1)	0.134 (1)
PtB	0.70403 (5)	0.21953 (5)	0.77140 (4)
Re1B	0.66027 (5)	0.31807 (5)	0.57329 (4)
Re2B	0.47923 (5)	0.27729 (5)	0.74898 (4)
Re3B	0.94526 (5)	0.22571 (5)	0.82238 (4)
OB	0.606 (1)	0.076 (1)	0.9683 (8)
O11B	0.663 (1)	0.5634 (9)	0.5166 (8)
O12B	0.889 (1)	0.351 (1)	0.4476 (8)
O13B	0.549 (1)	0.350 (1)	0.3959 (7)
O14B	0.637 (1)	0.0706 (9)	0.6324 (9)
O21B	0.582 (1)	0.4870 (9)	0.7465 (8)
O22B	0.377 (1)	0.211 (1)	0.9570 (7)
O23B	0.254 (1)	0.384 (1)	0.6870 (9)
O24B	0.398 (1)	0.054 (1)	0.766 (1)
O31B	0.783 (1)	0.3739 (9)	0.8839 (8)
O32B	0.866 (1)	0.024 (1)	1.0140 (9)
O33B	1.111 (1)	0.075 (1)	0.7710 (8)
O34B	1.006 (1)	0.408 (1)	0.6145 (8)
O35B	1.147 (1)	0.293 (1)	0.8993 (8)
CB	0.640 (1)	0.131 (1)	0.891 (1)
C11B	0.665 (2)	0.474 (1)	0.540 (1)
C12B	0.806 (2)	0.335 (1)	0.498 (1)
C13B	0.586 (1)	0.339 (1)	0.462 (1)
C14B	0.648 (1)	0.157 (1)	0.615 (1)
C21B	0.544 (1)	0.410 (1)	0.746 (1)
C22B	0.413 (1)	0.238 (1)	0.881 (1)
C23B	0.339 (1)	0.340 (1)	0.711 (1)
C24B	0.430 (1)	0.135 (1)	0.756 (1)
C31B	0.838 (1)	0.322 (1)	0.8615 (9)
C32B	0.894 (1)	0.102 (1)	0.948 (1)
C33B	1.050 (1)	0.130 (1)	0.786 (1)
C34B	0.984 (1)	0.346 (1)	0.692 (1)
C35B	1.073 (1)	0.270 (1)	0.871 (1)

The structures were solved by Patterson and Fourier methods, which revealed the locations of all the non-hydrogen atoms. In the case of compound **5** two crystallographically independent molecules were found. The refinements were carried out by full-matrix least squares. All atoms were treated anisotropically in both structures. The COD hydrogen atoms in **3** were located in ideal positions (C–H 0.95 Å; B = 5.0 Å^2), and all the hydride atoms were placed in computed positions, according to the Orpen's program,[13] with mean metal–H bond lengths of 1.85 Å (B = 4.0 Å^2). They were included in the structure factor calculations but not refined. The final difference-Fourier map showed only some residual peaks, not exceeding 1.3 e Å^{-3} in **3** and 1.5 e Å^{-3} in **5**, close to the metal atoms.

Weights were assigned according to the formula $w = 4F_o^2/\sigma(F_o^2)^2$, where $\sigma(F_o^2) = [\sigma(I)^2 + (pI)^2]^{1/2}/Lp$ (I and Lp being the integrated intensity and the Lorentz–polarization correction, respectively); p was optimized to 0.035 (**3**) and 0.030 (**5**). The handness of the crystal of **5** was tested by refining the two enantiomeric models. The final values of the agreement indices R

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and R_w are given in Table III. The atomic coordinates are reported in Tables IV and V, for compounds 3 and 5, respectively.

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Registry No. 1, 38887-05-7; **2**, 12130-66-4; **3**, 137546-76-0; **4a**, 126063-64-7; **4b**, 126186-21-8; **4c**, 126063-63-6; **5a**, 139495-14-0; **5b**, 139562-21-3; $[HRe(CO)_5]$, 16457-30-0; $[Re_2Pt(CO)_{12}]$, 91443-96-8; Pt, 7440-06-4; Re, 7440-15-5.

Supplementary Material Available: Tables of positional parameters for the hydrogen atoms, thermal parameters, and bond distances and angles for 3 and 5 (7 pages); final lists of observed and calculated structure factors moduli for 3 and 5 (44 pages). Ordering information is given on any current masthead page.

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Electronic Structure of Catalytically Important Palladium Complexes Studied by Photoelectron Spectroscopy

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The Pd 3d$_{5/2}$ core level binding energies have been measured by ESCA for a series of Pd(0) and Pd(II) compounds. Pd(0) complexes showed a considerable variation of these energies, depending on the ligands. In (π-allyl)Pd complexes, the energies were almost constant. This is explained by the donor-acceptor characteristics of the ligands. Differences in the reactivity of these complexes result from electron exchange between ligands via the metal atom, leaving its electron density unchanged.

Introduction

Complexes of palladium have become well-established tools in the synthesis of bulk chemicals as well as in elaborate synthetic strategies.[1] At the same time, the development of new reagents and methods relying on palladium is still one of the most productive fields in current organic chemistry. Usually, palladium compounds are assigned a formal oxidation number of 0, +I, +II, or +IV on the metal atom. If the formal oxidation number is kept constant, their reactivity and selectivity may be considerably altered by choice of the ligands on palladium.[2] For example, the addition of a quinone to the complexes **5–9** of the present work (cf. Figure 2), which substitutes one of the acetato or chloro ligands, results in an increased reactivity for nucleophilic substitution on the allyl moiety.[2c,3] However, apart from the observation that a chemical reaction occurs, there is no direct indication of an altered behavior of the metal atom. Oxidation numbers are of course a rather crude, formal model to describe the state of the metal atom. ^1H and ^{13}C NMR spectra of the organic ligands can provide some indirect indications,[3,4] but palladium itself is unfortunately not suitable for investigation by NMR spectroscopy,[5] which otherwise might reveal variations in its electronic state. For a limited number of palladium complexes, the redox potential of the metal atom has been determined.[6] The purpose of the present paper is to investigate a range of synthetically important complexes with ESCA (electron spectroscopy for chemical analysis) to provide information about the palladium state via the Pd 3d core level binding energies. This might be a possibility to probe directly the changes imposed on the metal atom by varying the ligands in palladium complexes with formally unaltered oxidation number. A variety of palladium(0) and palladium(II) complexes have been investigated.

The charge of the metal atom in a palladium complex results from the balance between donation and back-donation of electrons between the ligands and the metal atom.[1] The varying capacity of ligands to withdraw electrons from or to supply electrons to the metal atom emerges especially in mixed complexes. Thus, the oxidation potential of palladium in $Pd^0(quinone)(X)_2$ complexes has been shown to be independent of the quinone redox potential when the ligand X was a phosphine. When X was a diolefin, the oxidation potential increased with increasing redox potential of the quinone. This was explained by the higher capability of the phosphine ligand, as compared to an olefin, to supply electrons to the metal atom.[6]

ESCA has often been used as an experimental means of determining charges on the atoms in molecules and solids. The binding energy (E_B) of an electron in a certain core level of an atom in different chemical environments is in the first approximation directly proportional to the charge on the atom (q_{eff})[7]

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