

and $[\text{ZnTPPS}]_2$ (cf. Table I) was attributed^{2,3} to a combination of excitation transfer and charge transfer. Here it is shown that formation of free base-Zn porphyrin dimers and of free base-free base dimers has similar effects on zfs parameters. For reasons that will be outlined below, this suggests that we are probably dealing with localized triplet states.

In TPP systems the phenyl rings make an angle of 60–70° with the tetrapyrrole plane.⁶ Hence, for steric reasons, the macrocycles in TPP dimers must be rotated with respect to each other. As a consequence, excitation transfer should cause a reduction in E .⁷ This has been found for a Zn crown porphyrin⁴ (ZnTCP, cf. Table I). Charge transfer will reduce D .⁷ Formation of ZnTTAP/ZnTPPS does not affect D and E (cf. Table I). This indicates that the excitation energy is localized. It must be localized as well in ZnTTAP/TPPS and ZnTPPS/TTAP because the triplet state of the free base lies well below that of Zn porphyrins.⁸ The ZnTTAP/TPPS triplet lifetime is similar to that of TPPS and TTAP. This supports the localized triplet interpretation.⁷ The triplet ESR spectra of ZnTTAP/TPPS and ZnTPPS/TTAP are strikingly similar to those of TTAP/TPPS, [TPPS]₂,² and [TCP]₂.⁴ The logical conclusion is that in the free base dimers the excitation energy is localized as well. In free base TPP two of the pyrrole rings are turned out of the least-squares plane defined by the porphyrin core.⁶ The D -value reduction is attributed tentatively to a change in the degree of nonplanarity induced by dimerization. In Zn porphyrins the metal ion imparts a greater rigidity to the porphyrin core. For this reason dimerization is less likely to affect the structure.

The effect of TTAP/TPPS formation on triplet lifetime (cf. Table I) may be reconciled with the above interpretations by considering the great sensitivity of radiationless transitions to small changes in structure of the porphyrin core.⁹

The triplet energies of TTAP and TPPS (ZnTTAP and ZnTPPS) may differ enough to account for localized excitation in the dimers. In [TCP]₂ and [TPPS]₂ the energy levels of dimer constituents are degenerate, consequently one expects the triplet excitation to be shared. The finding that this is apparently not the case is puzzling and deserves further study.

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Models for the Triply Bridging Site in Chemisorption: The First Complex Containing the Pt₃(μ₃-H) Group and Evidence for Inversion of the Pt₃(μ₃-H) Unit and for Reversible Coordination of CO

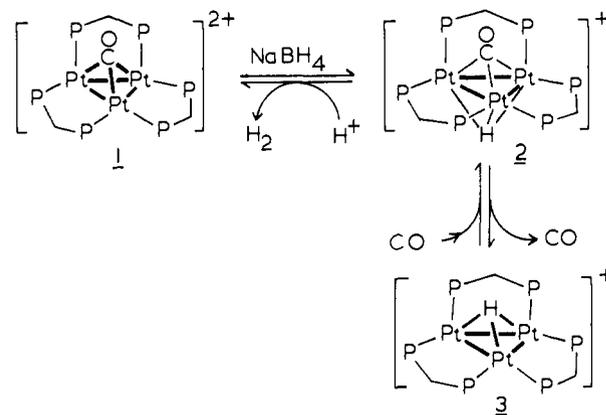
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Dissociative chemisorption of hydrogen on a Pt(111) surface leads to PtH, Pt₂(μ-H), and Pt₃(μ₃-H) linkages,^{1–4} but the Pt₃(μ₃-H) group has not been reported in platinum-hydride clusters which may be used as models for chemisorption.^{5–7} Following observations that the cation $[\text{Pd}_3(\mu_3\text{-CO})(\mu\text{-dppm})_3]^{2+}$, dppm = Ph₂PCH₂PPh₂, could bind halide ions at the triply bridging site

Scheme I



below the Pd₃ triangle⁸ and that the platinum analogue $[\text{Pt}_3(\mu_3\text{-CO})(\mu\text{-dppm})_3]^{2+}$ (1) could be prepared,⁹ attempts were made to synthesize a complex containing the desired Pt₃(μ₃-H) grouping.¹⁰

Reaction of 1 as the trifluoroacetate salt with NaBH₄ in methanol gave first $[\text{Pt}_3(\mu_3\text{-H})(\mu_3\text{-CO})(\mu\text{-dppm})_3]^+$ (2) and then $[\text{Pt}_3(\mu_3\text{-H})(\mu\text{-dppm})_3]^+$ (3) as monitored by ³¹P NMR spectroscopy¹¹ and 3 as the trifluoroacetate salt could be isolated after 24 h reaction times (Scheme I). The hydride signal in the ¹H NMR spectrum of 3 was observed at δ 4.16¹² as a septet due to coupling to six equivalent phosphorus atoms, ²J(PH) = 23 Hz, and with satellites due to coupling to ¹⁹⁵Pt [¹J(PtH) = 710 Hz] having the intensities expected for a Pt₃(μ₃-H) group.¹² The presence of a single hydride was confirmed by recording the ¹⁹⁵Pt and ¹⁹⁵Pt{¹H} NMR spectra of 3. An extra doublet splitting due to ¹J(PtH) ~ 710 Hz in the ¹H coupled spectrum was observed.¹³

The resonance due to the CH₂P₂ protons in the ¹H NMR spectrum of 3 at -60 °C appeared as an "AB" quartet [$\delta(\text{CH}^a\text{H}^b)$ 5.61, 5.02, ²J(H^aH^b) = 14 Hz], as expected for a nonplanar Pt₃(μ₃-H) complex.^{9,15} However, at room temperature a single resonance was observed, indicating a fluxional process in which an effective plane of symmetry containing the Pt₃P₆C₃ unit is introduced. Since the ³¹P NMR and the Pt-H resonance in the

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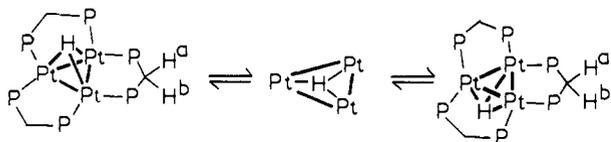
(10) Attempts to prepare Pd₃(μ₃-H) groups by reaction of $[\text{Pd}_3(\mu_3\text{-CO})(\mu\text{-dppm})_3]^{2+}$ with NaBH₄ were unsuccessful.

(11) ³¹P NMR data for 1, -15.1 [s, ¹J(PtP) = 3720, ³J(PP) = 170 Hz, PtP]; 2, -17.3 [s, ¹J(PtP) = 3019, ²J(PtP) = 200, ³J(PP) = 200 Hz, PtP]; 3, -11.1 [s, ¹J(PtP) = 3250, ²J(PtP) = 235, ³J(PP) = 175 Hz, PtP].

(12) The natural abundance of ¹⁹⁵Pt ($I = 1/2$) = 33.8%. Therefore, the abundances of isotopomers with 0, 1, 2, or 3 ¹⁹⁵Pt atoms is 29.0%, 44.4%, 22.7%, and 3.9% respectively. Superposition of spectra due to these species should give a 1:15:61:104:61:15:1 septet with lines separated by 0.5J(PtH). The outer lines were not observed, but the intensities of the inner lines were as expected. We cannot explain the unusual shift of the Pt₃(μ₃-H) proton but note that clusters with encapsulated hydride ligands may give low-field shifts, though other M₃(μ₃-H) groups give high-field shifts, and that there is a binuclear platinum hydride with δ 3. Forrow, N. J.; Knox, S. A. R.; Morris, M. J.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1983**, 234. Moore, D. S.; Robinson, S. D. *Chem. Soc. Rev.* **1983**, *12*, 415. Ciriano, M.; Green, M.; Howard, J. A. K.; Murray, M.; Spencer, J. L.; Stone, F. G. A.; Tsipis, C. A. *Adv. Chem. Ser.* **1978**, *167*, 111.

(13) ¹⁹⁵Pt NMR data for 1, -2685 [m, ¹J(PtP) = 3740, ¹J(PtPt) ≈ 380 Hz, Pt]; 2, -2440 [m, ¹J(PtP) = 3018, ²J(PtP) = 200, ¹J(PtPt) = 1800, ¹J(PtH) = 598 Hz, Pt]; 3, -2520 [m, ¹J(PtP) = 3250, ²J(PtP) = 240, ¹J(PtPt) ~ 2700, ¹J(PtH) = 710 Hz, Pt].

^1H NMR are unchanged, this process probably involves a direct inversion of the $\text{Pt}_3(\mu_3\text{-H})$ unit (eq 1).¹⁴ The activation energy



for this process is calculated to be $\Delta G^\ddagger = 50 \pm 1 \text{ kJ mol}^{-1}$ ($T_c = -24^\circ\text{C}$ at 100 MHz) and can be compared with $\Delta G^\ddagger = 46.5 \text{ kJ mol}^{-1}$ for inversion of the $\text{Pt}_2(\mu\text{-H})$ unit in the $[\text{Pt}_2\text{H}_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ ion.¹⁵

The cation **3** as the $[\text{PF}_6]^-$ salt could also be prepared by reduction of **1** with Na/Hg in tetrahydrofuran, followed by protonation with $\text{NH}_4[\text{PF}_6]$. It is possible that this reaction proceeds via the expected $[\text{Pt}_3(\mu\text{-dppm})_3]$ in which the planar Pt_3L_6 system is isolobal with cyclopropane.¹⁷

Complex **2** could be prepared by bubbling CO through a solution of **3** and could be converted back to **3** by flushing the solution of **2** with nitrogen for several hours. It was characterized by the ^1H , ^{31}P , and ^{195}Pt NMR spectra.^{11,14} The presence of the $\text{Pt}_3(\mu_3\text{-H})$ group was confirmed by the ^1H NMR at 20°C [$\delta -1.04$, septet, $^2J(\text{PH}) = 4.5$, $^1J(\text{PtH}) = 598 \text{ Hz}$] and by the ^1H -coupled ^{195}Pt NMR spectra,¹⁴ and the presence of CO was confirmed by the IR spectrum [$\nu(\text{CO}) = 1982 \text{ cm}^{-1}$, cf. $\nu(\text{CO})$ for **1** = 1750 cm^{-1}].⁸ At -60°C the $^1J(\text{PtH})$ coupling was reduced to 573 Hz and the chemical shift was $\delta -1.47$. Further characterization was obtained by treating **3** with ^{13}CO to give **2*** ($^* = ^{13}\text{CO}$ labeled). At -90°C , the hydride signal was at $\delta -1.67$ ($^1J(\text{PtH}) = 558 \text{ Hz}$ and a doublet splitting with $J(^{13}\text{CH}) = 40 \text{ Hz}$ was also observed), and in the ^{13}C NMR spectrum the carbonyl resonance was at $\delta 191$ as a septet with $^1J(\text{PtC}) = 434 \text{ Hz}$ [cf. $\delta 209$, $^1J(\text{PtC}) = 776 \text{ Hz}$ for **1**]¹⁸ with the intensities expected for a $\text{Pt}_3(\mu_3\text{-CO})$ group.¹² At room temperature only a broad resonance in the ^{13}C NMR spectrum was observed at $\delta 191$ without ^{195}Pt satellites and the coupling of ^{13}C to the $\text{Pt}_3(\mu_3\text{-H})$ resonance in the ^1H NMR was also lost. These data strongly indicate that reversible dissociation of CO from **2** occurs rapidly

(14) Migration of a proton through a triangle of metal atoms has been suggested to explain the reversible protonation of $[\text{Ni}_{12}(\text{CO})_{21}]\text{H}_{4-n}^{m+}$ in which the hydride ligands are interstitial and may also be involved in the protonation of $[\text{Co}_6(\text{CO})_{15}]^{2-}$ and in the migration of hydrogen atoms through metallic lattices. This appears to be the first direct evidence and the first time that the barrier to inversion has been determined. The data do not rule out transition states with lower symmetry, for example, with hydride bridging one edge, but these are less likely. A complex with an almost planar $\text{Er}_3(\mu\text{-H})$ group is known. Broach, R. W.; Dahl, L. F.; Longoni, G.; Chini, P.; Schulz, A. J.; Williams, J. M. *Adv. Chem. Ser.* **1978**, *167*, 93. Hart, D. W.; Teller, R. G.; Wei, C.-Y.; Bau, R.; Longoni, G.; Campanella, S.; Chini, P.; Koetzle, T. F. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 80. Evans, W. J.; Meadows, J. H.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 2015.

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(17) Mealli, C. *J. Am. Chem. Soc.* **1985**, *107*, 2245. We note that cyclopropane is protonated at an edge or corner, whereas $[\text{Pt}_3(\mu\text{-dppm})_3]^+$ is protonated at the center. This difference could have been predicted from the different MO sequences in the two cases.

(18) The presence of a $\mu_3\text{-CO}$ group in **2** is tentative at this stage. The NMR data show that, on the NMR time scale, the CO interacts equally with all Pt atoms, but the $\nu(\text{CO})$ value is unprecedented for a $\mu_3\text{-CO}$ group. The anomalous data can be rationalized in terms of an extremely weak $\text{Pt}_3(\mu_3\text{-CO})$ bond or it is possible that the CO in **2** is terminal or semi triply bridging but fluxional even at -90°C . **2** certainly represents the time-averaged structure. The remarkable changes in chemical shift and $^1J(\text{PtH})$ coupling constant for the $\text{Pt}_3(\mu_3\text{-H})$ resonance of **2** with temperature (vide infra) can be interpreted in terms of $\sim 20\%$ "effective" dissociation of CO at room temperature, assuming that the NMR parameters of this proposed complex are similar to those of **3**.

at room temperature and at temperatures as low as -60°C . However, the CH_2P_2 resonance of the dppm ligands was an "AB" quartet [$\delta(\text{CH}^a\text{H}^b)$ 5.43, 5.07, $^2J(\text{H}^a\text{H}^b) = 14 \text{ Hz}$] and samples containing both **2** and **3** gave separate, though broadened, NMR signals even at room temperature, showing that complete dissociation of the CO ligand from **2** is not fast on the NMR time scale. We suggest that effective reversible dissociation of the $\text{Pt}_3(\mu_3\text{-CO})$ bond occurs rapidly at room temperature but that the CO remains within the cage of phenyl rings surrounding the μ_3 -site and escapes only slowly into solution.¹⁸

The reaction $\mathbf{1} + \text{H}^- \rightarrow \mathbf{2} \rightleftharpoons \mathbf{3} + \text{CO}$ clearly defines a novel bimolecular mechanism of ligand substitution at the μ_3 -site, in which the intermediate **2** is sufficiently stable to be isolated.¹⁹

Acknowledgment. We thank NSERC (Canada) for financial support.

(19) The electron configuration in **2** is analogous to that in $[\text{Pt}_3(\mu_3\text{-SnCl}_3)_2(\text{cod})_3]$.¹⁷ However, when two different μ_3 ligands are present it seems that one is strongly and the other is weakly bound.⁸ In complex **2** H^- binds more strongly than CO, and it is the CO that is weakly bound. The lower value of $^1J(\text{PtH})$ also suggests a weaker PtH bond in **2** than in **3**. This mutual weakening of the bonds across the Pt_3 triangle is analogous to the trans influence in mononuclear complexes.

Photoelectron Spectra and Bonding in Cerocene, Bis(π -[8]annulene)cerium(IV)

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Quasi-relativistic SCF- $X\alpha$ scattered-wave calculations have recently indicated that cerocene (bis(π -[8]annulene)cerium(IV)) has an electronic structure unexpectedly similar to that of bis(π -[8]annulene)uranium(IV) (uranocene) and -thorium(IV) (thorocene).¹ Various theoretical criteria indicate a substantial covalency for the lanthanide sandwich including a degree of f-orbital interaction comparable to uranocene itself.² Such involvement of 4f orbitals in ring-metal bonding in an organo-lanthanide compound would be unusual and unprecedented but the simple existence of cerocene should alone be considered to be remarkable: the compound combines a strong reducing agent (the [8]annulene dianion rings) with a powerful oxidizing agent, cerium(IV). This combination would imply that the structure could not be that of a simple ionic cluster. We have reproduced the synthesis of cerocene reported by Greco, Cesca, and Bertolini;^{3,4}

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