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Geometrical characteristics from experiment and theory of isostructural complexes involving palladium and platinum–methyl bonds

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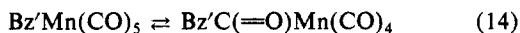
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k_{obsd} independent of the CO concentration. The results, which are reported in Figure 1 in the form of plots of $(k_{\text{obsd}})^{-1}$ vs. $[\text{OPPh}_3]^{-1}$, clearly conform to eq 13 and provide convincing support for the dissociative trapping mechanism B.¹⁰ The plots in Figure 1 yield the values $(k_{-5}k_{-10})/(k_5k_{10}k_{11}) = (1.36 \pm 0.04) \times 10^2 \text{ M s}$ and $(k_{-5} + k_{10})/(k_5k_{10}) = (2.58 \pm 0.09) \times 10^2 \text{ M s}$.

According to the mechanistic interpretation of eq 5, 10, 11, and 7, the intercepts of the plots in Figure 1 $(k_{-5}k_{-10})/(k_5k_{10}k_{11})$ -[HMn(CO)₄P] correspond to establishment of the equilibrium of eq 14 and trapping of the equilibrium concentration of Bz'C-



(=O)Mn(CO)₄ (3) by HMn(CO)₄P. This predicts that the magnitudes of the intercepts of such plots should be independent of the identity of the catalytic nucleophile. Preliminary experiments with other catalysts including OPBu₃, CH₃CN, and THF confirm this prediction and support the same mechanistic interpretation of earlier observations of the promotion of CO migratory insertion by other donor solvents and nucleophilic reagents.^{2,3} We conclude that the role of such nucleophiles is not to stabilize the coordinately unsaturated acyl intermediates (e.g., 3) but rather to catalyze their formation.

Further experiments to determine some of the individual rate constants in eq 12 and to extend these studies to other catalysts and other CO migratory insertion reactions (notably of CpMo(CO)₃R and CpFe(CO)₂R) are in progress.

Acknowledgment. We thank the National Science Foundation and the Sun Oil Co. for grants in support of this research. The NMR facilities were supported in part through the University of Chicago Cancer Center Grant NIH-CA-14599.

(10) In the plot of [intercept]⁻¹ vs. [HMn(CO)₄P]⁻¹ (inset in Figure 1) the point for the lowest HMn(CO)₄P concentration (0.031 M) falls below the line passing through the other points. This is attributable to a contribution from the trapping of 3 by CO which becomes significant under these conditions. In accord with this, up to 10% Bz'C(=O)Mn(CO)₅ was observed to form in these experiments; at higher HMn(CO)₄(PMe₂Ph) concentrations the yield of Bz'C(=O)Mn(CO)₅ was much lower ($\leq 5\%$). Such additional trapping by CO effectively increases the value of the trapping rate constant k_{11} . In accord with eq 12 and Figure 1, this reduces the intercept of the plot of $(k_{\text{obsd}})^{-1}$ vs. $[\text{OPPh}_3]^{-1}$ but does not affect the slope. Under the circumstances the point for 0.031 M HMn(CO)₄P was omitted from the calculation of $(k_{-5}k_{-10})/(k_5k_{10}k_{11})$.

Geometrical Characteristics from Experiment and Theory of Isostructural Complexes Involving Palladium- and Platinum-Methyl Bonds

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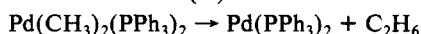
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Oxidative addition and reductive elimination reactions play a critical role in some of the most important processes in organometallic chemistry.¹ In such reactions, Pd(II) and Pt(II) systems often show different chemistry. As one example, reductive coupling of C-C bonds from Pd(II)²



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Table I. Experimental and Theoretical Bond Distances (Å) in M(CH₃)₂(PR₃)₂ Systems

	exptl M(CH ₃) ₂ [P- (C ₆ H ₅) ₂ CH ₃] ₂	theoretical M(CH ₃) ₂ - (PH ₃) ₂
(Pt-C)	2.120 (4) ^a	2.06
(Pd-C)	2.090 (2)	2.02
Δ _C	0.030 (4)	0.04
(Pt-P)	2.284 (1)	2.46
(Pd-P)	2.323 (1)	2.50
Δ _P	-0.039 (1)	-0.04

^a Estimated standard deviation of the mean.

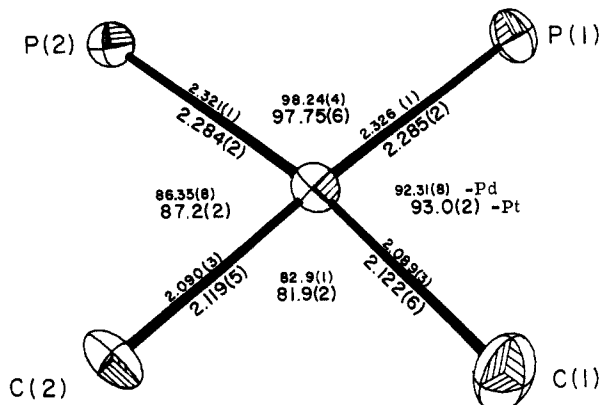


Figure 1. Coordination sphere around the metal in *cis*-M(CH₃)₂[P-(C₆H₅)₂CH₃]₂, M = Pt, Pd. Bond distances and angles for the Pd complex are in smaller type. Thermal ellipsoids at the 50% probability level are shown.

has been shown to be concerted.² However, Pt(CH₃)₂(PR₃)₂ complexes are very stable and have never been reported to undergo reductive elimination.³ Indeed, Pt dialkyls tend to decompose through β-hydride elimination⁴ if this pathway is available, even though direct C-C reductive coupling is thermodynamically favored. This dramatically different chemistry for very similar Pd(II) and Pt(II) systems led us to pursue the present experimental and theoretical studies⁵ on the geometries and energetics for the species *cis*-M(CH₃)₂(PR₃)₂, where M = Pd or Pt.

With an interest in correlating metrical information with reactivity, we undertook an X-ray structural study of the complexes *cis*-M(CH₃)₂[P(C₆H₅)₂CH₃]₂, where M = Pd or Pt. Prior to this study, no structural comparisons of Pt and Pd alkyl complexes had been made. In fact, the literature contains only two reports⁶ of structures with Pd-Me bonds. The present complexes were chosen because of their relative stability and simplicity. *cis*-M(CH₃)₂[P(C₆H₅)₂CH₃]₂, M = Pd or Pt, are strictly isostructural,⁷

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(7) Selected data for the X-ray structure determinations. Pd complex: C_{2h}⁵-P₂/c, Z = 4, a = 8.882 (3) Å, b = 26.500 (7) Å, c = 11.168 (4) Å, β = 108.27 (4)°, V = 2496 Å³ at -162 °C. 4799 independent F_o² values used to determine 280 variables—all nonhydrogen atoms anisotropic, H atoms, including methyl H atoms located and idealized. R(F²) = 0.038; R(F) for F_o² > 3σ(F_o²) = 0.028. Pt complex: C_{2h}⁵-P₂/c, Z = 4, a = 8.859 (4) Å, b = 26.302 (10) Å, c = 11.215 (5) Å, β = 108.60 (2)°, V = 2476 Å³ at -162 °C. 7678 independent F_o², same model as for Pd. R(F²) = 0.078; R(F) = 0.049. Details will appear elsewhere: Wisner, J. M.; Bartczak, T. J.; Ibers, J. A., unpublished results.

so a comparison of metrical parameters in these two complexes is not complicated by solid-state effects. The theoretical studies examined $M(R_1)(R_2)(PH_3)_2$ complexes, $M = Pd, Pt$; $R_1, R_2 = H, CH_3$.

These theoretical and experimental studies were completed simultaneously and independently (Table I). Of particular interest are the differences in bond lengths, $\Delta_C = (Pt-C) - (Pd-C)$ and $\Delta_P = (Pt-P) - (Pd-P)$, which are of opposite sign.⁸ Figure 1 illustrates the inner coordination sphere in these complexes and presents pertinent bond distances and angles. Coordination about the central metal in both complexes is essentially square-planar with a very slight tetrahedral distortion. Chemically equivalent bond distances in both structures agree within the estimated standard deviations. Average distances are tabulated in Table I. No structures of comparable accuracy have been reported that permit a reliable estimate of Δ_C ; there are a few structures where Δ_P has been determined to about the same level of significance [e.g., $M[P(Ph)(t-Bu)_2]_2$, $Pt-P = 2.252$ (1), $Pd-P = 2.285$ (2) Å, $\Delta_P = -0.033$ (2) Å].⁹

One would expect that the opposite sign found for Δ_P and Δ_C is connected with some change in the electronic character of the wavefunctions for Pd vs. Pt. This could be considered consistent with the general trend in the literature that "hard" or σ -bonding ligands, such as alkyls and halides, tend to show longer bonds to third-row transition metals than to their second-row analogues, whereas the opposite is true for "soft" or π -bonding ligands, such as phosphines. We will now use the wavefunctions from theory to analyze more precisely the origin of geometric changes from Pd to Pt.

In fact, detailed comparisons of the electronic structure for Pd-C vs. Pt-C bonds do not provide an explanation of the short Pd-C bond length relative to Pt-C. Thus, calculations on $M(CH_3)_2$ yield $Pt-C = 1.97$ Å vs. $Pd-C = 1.96$ Å and $C-Pt-C = 98^\circ$ vs. $C-Pd-C = 92^\circ$, which can be compared with 2.06 Å, 2.02 Å, 89° , and 81° calculated for $M(CH_3)_2(PH_3)_2$. All four complexes involve M-C bonds that are essentially covalent with one electron in a C sp^3 orbital and the other in an M spd hybrid. [$Pt(CH_3)_2(PH_3)_2$ $Pt = s^{0.23}p^{0.10}d^{0.49}C^{0.17}$ and $CH_3 = (sp)^{-0.03}d^{0.13}C^{0.18}p^{0.71}$; $Pd(CH_3)_2(PH_3)_2$ $Pd = s^{0.17}p^{0.07}d^{0.49}C^{0.24}$ and $CH_3 = (sp)^{-0.02}d^{0.15}C^{0.18}p^{0.68}$; $Pt(CH_3)_2$ $Pt = s^{0.27}p^{0.01}d^{0.62}C^{0.10}$ and $CH_3 = (sp)^{0.00}d^{0.15}C^{0.14}p^{0.70}$; $Pd(CH_3)_2$ $Pd = s^{0.16}p^{0.03}d^{0.55}C^{0.24}$ and $CH_3 = (sp)^{0.01}d^{0.20}C^{0.28}p^{0.52}$.] The effective electronic configuration on the metal is d^9s^1 , affording two singly occupied orbitals (one s, one d) that are hybridized to form two sd hybrids suitable for bonding the two methyl groups. The M orbital of Pd has less sp character (0.24 Pd vs. 0.33 Pt) and concomitantly more charge transfer to the CH_3 (0.24 Pd vs. 0.17 Pt). Such a difference is not surprising since Pt prefers the d^9s^1 atomic configuration, whereas Pd prefers d^{10} . Unfortunately these differences do not account for our mystery. The $M(CH_3)_2$ bonds have nearly the same bond distances but similar differences in hybrid character. Analysis of Mulliken populations for the Pd and Pt complexes shows less M sp character on Pd (by 0.40 e) for $M(CH_3)_2(PH_3)_2$, but the same comparison for $M(CH_3)_2$ shows a similar decrease (by 0.37 e).

Because of the large increase in relativistic effects from Pd to Pt, the valence s electrons on Pt are greatly stabilized with respect to valence d electrons, leading to a d^9s^1 ground state for Pt (with d^{10} higher by 11.0 kcal/mol),¹⁰ whereas Pd has a d^{10} ground state (with d^9s^1 higher by 21.9 kcal/mol).¹⁰ Similarly, the electron affinity¹¹ of $Pt(d^{10})$ is 2 eV greater than for $Pd(d^{10})$. Since $Pt d^{10}$ is a far better Lewis acid than $Pd d^{10}$, it is not surprising that $Pt(PH_3)_2$ has a much shorter bond distance than $Pd(PH_3)_2$. (From

theory $Pt-P = 2.32$ Å vs. $Pd-P = 2.41$ Å for linear complexes.) Addition of the two methyl groups forces the phosphines together (calculated $P-Pt-P = 101^\circ$, $P-Pd-P = 98^\circ$) and promotes the metal from d^{10} toward d^9s^1 . Both these effects tend to increase the M-P distance, but the Pt-P remains 0.04 Å smaller. Comparing $M(CH_3)_2$ and $M(CH_3)_2(PH_3)_2$, we find that the Pt- CH_3 bond distance increases by 0.09 Å, while the Pd- CH_3 bond distance increases by only 0.06 Å. The smaller increase for Pd can be understood in terms of the smaller PH_3-CH_3 interactions that result from the longer Pd- PH_3 bond distance. This explanation that steric effects dominate the differences in Δ_C between Pd and Pt is consistent with the fact that the respective $P \cdots C(Me)$ distances in the two compounds are essentially equal [3.038 (6) and 3.197 (7) Å for Pt and 3.022 (3) and 3.189 (3) Å for Pd]. Additional structural studies of comparable accuracy would be valuable in ascertaining the generality of this explanation in terms of both electronic and steric effects.

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On the Freeness of the Metaphosphate Anion in Aqueous Solution

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The mechanism of hydrolysis of phosphate monoesters remains uncertain in spite of intensive study in a number of laboratories.¹ On the basis of pH-rate profiles, the involvement of a hypothetical metaphosphate ion in the aqueous solvolysis of these compounds was first proposed 3 decades ago by Westheimer² and by Bunton.³ Bunton^{4a} and Kirby^{4b} further supported this mechanism with studies on the hydrolysis of substituted phenyl phosphates at a number of pH values. Subsequent medium and product studies uncovered evidence of *free* metaphosphate ion in aprotic media,⁵ and its direct observation in the gas phase by negative ion mass spectrometry was reported shortly thereafter.⁶

Recent investigations, on the other hand, have tended to emphasize that these reactions cannot generate a *completely free* metaphosphate ion intermediate, at least not in protic media. The hydrolysis of esters chiral at phosphorus by ^{16}O , ^{17}O , and ^{18}O substitution proceeded with inversion of configuration.⁷ Transfer of a phosphoryl residue from a pyridinium^{8a} or quinolinium^{8b}

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