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The Isotopic Trans Effect

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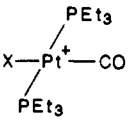
D is found to have a higher trans influence than H, as reflected in ^1J(Pt,P) and ^1J(Pt,C) coupling constants in *trans*-$[HPt(PEt_3)_2L]^+$ (L = ^{13}CO or PEt_3) and the PtD analogues. The isotopic effect on trans ligand labilization is also discussed in the case of $[IrH_2(Me_2CO)_2(PPh_3)_2]^+$. Molecular H_2 (D_2) complexes are proposed as intermediates in the deuteration of the iridium complex.

We are currently exploiting NMR methods for distinguishing between classical (MH_xL_y) and nonclassical ($M(H_2)_xH_yL_z$) structures for polyhydrides.[1] Many polyhydrides are at the fast-exchange limit, and the molecular hydrogen and terminal hydride ligands show averaged resonances at all accessible temperatures.[2] Two methods look promising: (i) T_1 measurements[1] and (ii) isotopic perturbation of resonance,[2b,3] which results from the introduction of deuterium into the polyhydride under study. In order to be able to interpret our results, we need measurements on unambiguously classical hydride complexes. We previously reported T_1 measurements of such classical hydrides,[4] and we now report the effect of deuterium substitution on the chemical shifts and coupling constants in the complexes **1** and **2**. This experiment is essentially a determination of the differential isotopic trans influence of H and D.[5] For completeness we also looked at the isotopic trans effect of deuterium substitution on the rate of acetone loss from **3**.



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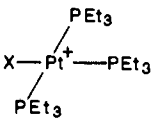

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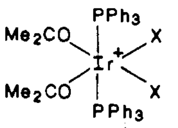

3

a, X = H; **b**, X = D

The Isotopic Trans Influence

Since ^1J(Pt,P) and ^1J(Pt,C) coupling constants are usually so large, we felt that **1** and **2** would be good species in which to look for an isotope effect. The values obtained are shown in Table I. In each case the coupling constant of the bond trans to H is higher than that trans to D by ca. 1%. (**1**, 1.0%; **2**, 1.2%).

The usual explanation[6] for such differences probably applies: the different average internuclear separation for Pt–H compared to Pt–D. This difference has its origin in the anharmonicity of the Pt–H potential well and the different zero point energies of Pt–H vs. Pt–D, as has been proposed[7b] in the case of C–H(D). The experimentally determined differences[7] between X–H and X–D bond distances for the heavier elements are rather similar and average 0.005 Å (X–H being the longer). This is in the right direction to account for the observed isotopic trans influence, because we would expect the D atom to spend more of its time nearer the metal than would the H atom. If the trans influence of L_i falls as the M–L_i distance increases, which is entirely reasonable, then this accepted mechanism can account for the observed isotope effect. The cis Pt–P coupling constants were essentially unaffected by the isotopic substitution (**1a**, 2516.3 (±1.5) Hz, **1b**, 2514 (±1.5) Hz). Similarly, $^2J(P_{cis}P_{trans})$ remained at 20.0 Hz throughout. After adjustment for the difference in gyromagnetic ratios, there was no difference in the values of ^1J(Pt,H) and ^1J(Pt,D) (**1a**, 790 Hz).

Table I. NMR Data for **1** and **2**

datum	**1a**	**1b**	**2a**	**2b**	isotopic diff[a]
^1J(Pt,C) (±0.6), Hz			996.2	986.3	−1.0%
$\delta(^{13}C)$ (±0.01)			183.38	183.54	+0.16%
$^1J(PtP_{trans})$ (±1.5), Hz	2055.6	2031.5			−1.19%
$^1J(Pt,P_{cis})$ (±1.5), Hz	2516.3	2513.9			−0.1%
$\delta(P_{trans})$ (±0.01)	14.95	14.94			*b*
$\delta(P_{cis})$ (±0.01)	18.11	18.08			*b*

[a] Differences shown in percent for coupling constants and in ppm for chemical shifts on going from H to D. [b] Essentially unchanged, within experimental error on goint from H to D.

Table II. Line Broadening Data for **3a** and **3b**[a]

complex	T,[b] K	$\omega_{1/2}$, Hz	$\omega_{1/2}$(cor),[c] Hz	k,[d] s^{-1}	k_H/k_D[7c]
3a	276	11.07	8.88	27.90	1.12
3b	276	10.13	7.94	24.94	
3a	278	12.92	10.63	33.40	1.18
3b	278	11.19	9.00	28.27	
3a	280	16.36	14.17	44.52	1.12
3b	280	14.88	12.69	39.87	
3a	281	18.14	15.94	50.08	1.13
3b	281	16.25	14.06	44.17	
3a	283	21.58	19.39	60.92	1.11
3b	283	20.32	18.13	56.96	

[a] δ(free Me_2CO) = 2.11; δ(bound Me_2CO) = 1.42. [b] Useful data could only be obtained in this temperature range. [c] Corrected for the natural line width. [d] Rate constant for leaving the coordination site.

In the case of **1a** there is essentially no isotope effect on the ^{31}P chemical shifts (P_{cis} 0.03 ppm and P_{trans} 0.01 ppm (± 0.02 ppm) shifts to low field). On the other hand, in **2** the isotopic substitution of H for D does have a significant effect on the ^{13}C chemical shift: the resonance moves 0.16 ppm to low field. While the chemical shift of an atom directly bonded to H (D) is known to show an isotopic shift,[8a] the two-bond effect is usually less than 0.1 ppm and, usually, occurs in the high-field direction,[8a] the reverse of the direction we observe here. In the literature examples, the effect is transmitted through a carbon chain, not a platinum atom as here. The unusual sign of the isotope shift may therefore be another manifestation of the isotopic trans influence. In confirmation of this view, Lewis and Johnson[8b] have reported the ^{13}C chemical shifts of a number of carbonyls related to **2** and have generally seen low-field shifts for high-trans-influence ligands.

Secondary Isotope Effects on Ligand Substitution

We were also interested in the kinetic phenomena associated with the substitution of D for H. Halpern[9] has reported a sec-

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ondary isotope effect in the substitution of pyridine (py) for Cl^- in *trans*-$[PtHCl(PR_3)_2]$. He found a k_H/k_D of 1.4. He argued that this unusually high value implied a large change of ν(Pt–H) in the transition state. The substitution is likely to be associative, so the transition state in question would have a stereochemistry intermediate between a square plane and a trigonal bipyramid with Pt–H in the equatorial plane. This might well lead to a significant change in ν(Pt–H).

We looked at an octahedral complex **3**, to compare it with the result for square-planar Pt, discussed above. In this complex, the acetone ligands exchange with free acetone by a dissociative mechanism. ^1H NMR line-broadening methods have been applied to this problem by Moore, et al.[10] We studied this exchange in **3a** and **3b** (Table II) and observed a k_H/k_D of 1.13, much smaller than the value observed for Pt.[11] It is interesting to see that the apparent trans effects are in the order H > D while the trans-influence order is D > H. The difference reflects the different mechanisms operating in the two cases. The isotopic trans influence probably arises largely from the different M–H(D) average internuclear distances, and the kinetic isotope effect, from the differences in vibrational frequencies between ground and transition states.

We also found that the broadening of the bound Me_2CO was unaffected by altering the amount of free acetone present, while broadening of the free acetone peak was affected by the amount of free acetone present. This observation confirms Moore and Morris'[10] conclusion that the exchange is dissociative. We therefore took the broadening of the resonance for coordinated Me_2CO as the best measure of the rate we were interested in, the rate of Me_2CO departure from the complex.

This result implies that the change in ν(M–H) on going to the transition state is much smaller than is the case for the displacement of Cl^- from $[HPtCl(PR_3)_2]$ by pyridine. There are two possible reasons. First, acetone is a weakly bound ligand and so its departure is likely to perturb the trans Ir–H bond much less than would be the case for the departure of a strongly bound ligand. Second, the dissociative mechanism probably implies relatively little stereochemical rearrangement in the transition state, compared to the platinum case.

Deuteration Studies

The deuteration of the acetone complex **3** was of particular interest. We found that the protio complex **3a** as a powder exchanges very rapidly with D_2 to give the deuterio analogue **3b** in the solid state at room temperature.[12] This shows the high permeability of the microcrystals to molecular hydrogen. More recently we have found that H_2 can readily replace coordinated solvents from Ir(III) complexes to give dihydrogen hydride species.[13] The complex $[IrH_2(H_2)_2\{P(C_6H_{11})_3\}_2]^+$, closely related to **3**, has been observed and characterized at low temperature. As mentioned in the introduction, the dihydrogen protons tend to undergo rapid exchange with any terminal hydrides also present in the polyhydride.

It is not yet clear whether this exchange goes by oxidative addition via a classical hydride tautomer or whether it is simple proton transfer between the $M(H_2)$ and MH groups.[13] The latter mechanism should be considered in cases where exchange occurs, but oxidative addition is unlikely (d^0 hydrides, lanthanide and actinide hydrides).

$$[IrH_2S_2L_2]^+ \rightleftharpoons [IrH_2S(D_2)L_2]^+ \rightleftharpoons [IrD_2S(H_2)L_2]^+ \rightleftharpoons [IrD_2S_2L_2]^+$$

Experimental Section

Deuteriotris(triethylphosphine)platinum(II) Tetraphenylborate. $[PtH(PEt_3)_3]BPh_4$, prepared by the literature procedure,[14] was deuterated by treating 0.2 mmol of the complex with a 0.1 M solution of KOMe in MeOD (2 mL) at 25 °C for 12 h. The product was precipitated with Et_2O, filtered out, and dried in vacuo. The procedure was repeated was repeated, and the product was recrystallized from CH_2Cl_2/Et_2O. The final deuteration reached ca. 99%. IR: ν(Pt–D) = 1522 cm^{-1}, ν(Pt–H) = 2120 cm^{-1}.

Deuterio([^{13}C]carbonyl)bis(triethylphosphine)platinum(II) Perchlorate—*Caution*! Perchlorates are shock-sensitive, but no other counterion we tried gave satisfactory solubility. $[PtD(^{13}CO)(PEt_3)_2]ClO_4$ was prepared by the literature method,[15] involving substitution of CO for Cl^- in the corresponding chloride, but using ^{13}CO instead of CO and $[PtDCl(PEt_3)_2]$ instead $[PtHCl(PEt_3)_2]$ as starting materials. The $[PtDCl(PEt_3)_2]$ was obtained by the literature method[5] by exchanging the hydrido complex with MeOD containing DCl (0.1 M) as catalyst. The degree of deuteration was 70% D and 90% ^{13}C. IR: **2a**, $\nu(^{13}C–O)$ = 1958 cm^{-1}, $\nu(^{12}C–O)$ = 2043 cm^{-1}; **2a**, ν(Pt–H) = 2167 cm^{-1}; **2b**, ν(Pt–D) = 1556 cm^{-1}.

Dideuteriobis(acetone)bis(triphenylphosphine)iridium(III) Tetrafluoroborate. Method A. This complex was prepared by the method of ref 16 but using D_2 instead of H_2. Rather than bubble D_2 through the solution, we maintained the solution under 1 atm of D_2.

Method B. Powdered $[IrH_2(Me_2CO)_2(PPh_3)_2]BF_4$ was found to exchange with D_2 on passing this gas over the solid at room temperature. The degree of deuteration of the sample used was 87%.

NMR. NMR data were obtained on a Bruker WM-250 or -500 spectrometer at 25 °C in acetone-d_6 (**1**), $CDCl_3$ (**2**), or CD_2Cl_2 (**3**). The resolution used in each case led to the experimental errors listed in Table I. For the data of Table II, a 32K data collection over 2000 Hz gave a resolution of 0.12 Hz/point. The ^1H NMR data were recorded at 250 MHz, the ^{13}C NMR at 62.9 MHz, and the ^{31}P NMR at 202.5 MHz. Decoupling experiments were carried out to confirm the assignments of the couplings. The line-broadening experiments were carried out by the method of ref 6.

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