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A ^{1}H NMR Study of *trans*-Hydrido(1,3-diaryltriazenido)bis(triphenylphosphine)platinum(II) Complexes

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In the course of studying the chemistry and the mode of coordination of the triazenido ligand, $(RN\dot{-}N\dot{-}NR')^-$, in transition metal complexes [1], here we report a ^{1}H NMR study of *trans*-$[PtH(p\text{-}XC_6H_4N{-}N{=}NC_6H_4X\text{-}p)(PPh_3)_2]$ (I) (X = Cl, F, H, and CH_3). Complexes (I) were prepared in all cases by dissolving *cis*-$[PtCl_2(PPh_3)_2]$ with hydrazine hydrate in ethanol and then treating the yellow solution with an excess of ArNH–N=NAr, as already described [2].

The ^{1}H NMR spectra were recorded in $CDCl_3$ at –30 °C because the complexes are rather unstable at room temperature; from room temperature down to –60 °C the high field NMR spectrum for hydrogen bonded to platinum consists of three triplets centered at *ca.* τ_{24} with $J_{P-H} \simeq 13.5$ Hz and $J_{Pt-H} \simeq 900$ Hz (See Table). It is interesting to observe that the NMR spectrum for the thiolate complexes *trans*-$[PtH(SC_6H_4X\text{-}p)(PPh_3)_2]$ (II) shows only one "triplet", because of the absence of the coupling with the P nuclei, centered at *ca.* τ_{30}, with $J_{Pt-H} \simeq 970$ Hz [3]. These observations suggest that the rapid exchange of a PPh_3 molecule in the series of complexes (II) is not occurring in the series of complexes (I).

Analogously to what was found for the series of complexes (II), a good linear correlation is obtained when J_{Pt-H} is plotted against the Hammett substituent parameter, σ_p (See Figure 1). Somewhat surprisingly, in the series of complexes (II), τ_H was insensitive to X, contrary to what is observed for the series (I), where τ_H correlates well when plotted against σ_p (See Figure 2).

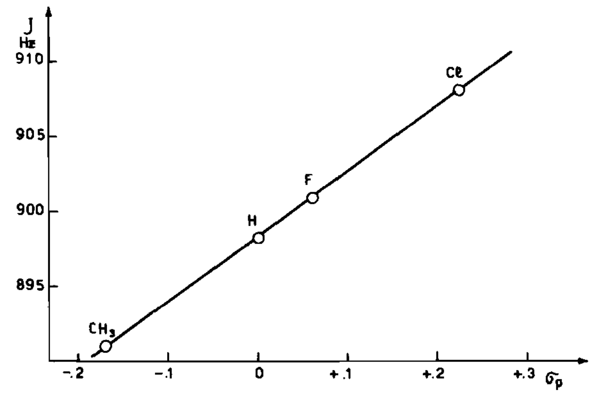

Fig. 1. Plot of J_{Pt-H} *vs.* σ_p.

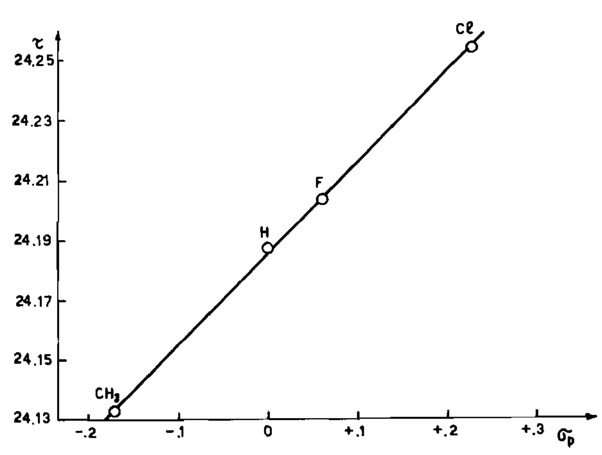

Fig. 2. Plot of τ_{Pt-H} *vs.* σ_p.

For another series of complexes *trans*-$[PtHL(PEt_3)_2]$ (III), where L is a *o*-, *m*-, or *p*-substituted benzoato-ligand, a good linear correlation was found when each of the parameters ν_{Pt-H}, τ_{Pt-H}, or J_{Pt-H}

TABLE . NMR and IR Data.

Complex	τ_{Pt-H}	J_{Pt-H} Hz	J_{P-H} Hz	ν_{Pt-H} ^{d,e} cm^{-1}
$PtH(ClC_6H_4N{-}N{=}NC_6H_4Cl)(PPh_3)$	24.25	909	13.5	2147(2155)
$PtH(FC_6H_4N{-}N{=}NC_6H_4F)(PPh_3)_2$	24.20	901	13.5	2142(2153)
$PtH(C_6H_5N{-}N{=}NC_6H_5)(PPh_3)_2$	24.19	898	14	2153(2153)
$PtH(CH_3C_6H_4N{-}N{=}NC_6H_4CH_3)(PPh_3)_2$	24.13	891	14	2143(2151)
$PtH(SC_6H_5)(PPh_3)_2$ ^{a}	29.87	969	13.4	– (2127)
$PtH(O_2CC_6H_5)(PEt_3)_2$ ^{b}	31.918	1179.1	15.65	2230 –
$[PtH(NH_2NHC_6H_5)(PPh_3)_2](BF_4)$ ^{c}	26.68	1077	13	2210 –
$[PtH(C_6H_5NHNC_3H_6)(PPh_3)_2](BF_4)$ ^{c}	27.36	1041	13.5	2220

^{a,b,c}See reference 3, 4, and 6, respectively. ^{d}In KBr pellet or Nujol mull. ^{e}In $CHCl_3$.

was plotted against each of the other parameters and each parameter varied linearly with pK_a of the parent benzoic acid [4]; moreover J_{Pt-H} varied linearly with σ_p [3].

The factors influencing ν_{Pt-H}, τ_{Pt-H}, and J_{Pt-H} for the series of complexes (II) and (III) have been already discussed [3, 4]. It was stated that as pK_a decreases, because of the higher drift of electron density away from the metal, there is (i) a shortening of the metal–hydrogen bond, (ii) an increase in the s-character of the bond, and (iii) an increase in the amplitude of the Pt(6s) orbital at the nucleus. It was concluded that (i) the shortening of the Pt–H bond length (with consequent increasing of ν_{Pt-H}) may be the main cause of the variation in τ_H (in view of the good correlation between τ_H and ν_{Pt-H}) and that (ii) the variation in the s-character of the bond is the most likely source of the variation in J_{Pt-H}. In the series of complexes (I), τ_H and J_{Pt-H} increases with ν_{Pt-H}, however, owing to the relative size of the error in determining ν_{Pt-H}, it is not possible to seek any close correlation, even though this cannot be ruled out (See the IR data in the Table, taken in $CHCl_3$). Thus the above conclusions suggested for the series (III) may hold for the series (I) as well.

It is interesting to compare ν_{Pt-H}, τ_{Pt-H}, and J_{Pt-H} in the series of complexes (I), (II), and (III) in order to correlate the *trans*-influence of the ligand in *trans* position to the hydride ligand. Complexes (I) and (II) present comparable values for ν_{Pt-H} and J_{Pt-H} but different values for τ_H. As already pointed out, unlike ν_{Pt-H} and J_{Pt-H}, τ_H does not really indicate primarily variation in the Pt–H bond itself but rather variation at the platinum atom [5]. Consequently, since the *trans*-influence of a ligand as indicated by τ_H is at variance with that indicated by ν_{Pt-H} and J_{Pt-H}, the latter parameters provide a better indication that the triazenido- and the thiolate-ligand present a comparable *trans*-influence. Since the series of complexes (III) present higher ν_{Pt-H} and J_{Pt-H} values than those of the series (I) and (II), it can be concluded that the carboxylato-ligand presents a smaller *trans*-influence than the triazenido and thiolate ones.

At last, the comparison between ν_{Pt-H} and J_{Pt-H} values for complexes (I), *trans*-$[PtH(NH_2NHAr)(PPh_3)_2][BF_4]$ and *trans*-$[PtH(ArNHNC_3H_6)(PPh_3)_2][BF_4]$ [6], having a nitrogen-donor ligand, indicates that the latter ones present a smaller *trans*-influence. Since it is generally observed that the *trans*-influence of a ligand increases as its σ-donor ability increases [7], it follows that the anionic triazene ligand is a better σ-donor than the neutral ones mentioned above.

References

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