Carbon-13 Nuclear Magnetic Resonance Spectra of some Carbon-13 Monoxide Derivatives of Platinum(II)

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^{13}C N.m.r. chemical shifts, δ, and $^{1}J(^{195}Pt-^{13}C)$ coupling constants have been obtained for a series of anionic, neutral, and cationic platinum(II) carbonyl complexes incorporating ^{13}CO. In the series [PtX(CO)L,L′] with the group X *trans* to the labelled carbonyl group, for constant X a decrease in δ has been observed for the ^{13}CO with increasing negative charge on the complex. Little variation in δ has been observed with change in the *cis*-ligand. Two ranges of values for $^{1}J(^{195}Pt-^{13}C)$ have been obtained for variation of *trans*-group X: for ligands with high *trans*-influence the coupling is in the range 960—990 Hz, whilst for ligands with low *trans*-influence the coupling falls in the region 1 658—1 817 Hz.

THE nature of the metal–carbon bond in organometallic molecules has frequently been elicited from changes in i.r. frequencies induced by variation in co-ordinated ligand groups. This has been particularly useful for molecules containing the co-ordinated carbonyl group as this group absorbs in the region of the i.r. spectrum where interactions with other vibrational modes are minimised. In addition, metal–ligand bonding has been studied more directly by considering changes in specific metal–ligand properties such as the variation in n.m.r. coupling constants in a metal–ligand bond, for example ^{1}J(M–H) in metal hydrides and ^{1}J(M–P) in metal phosphine derivatives. Recently, metal–carbon coupling constants obtained from ^{13}C n.m.r. spectra of σ-bonded species have been utilised to study the metal–carbon bond.[1,2]

^{13}C N.m.r. (δ/p.p.m., J/Hz) and i.r. spectroscopic data (cm^{-1})

Complex	δ(CO) [a]	^{1}J(Pt–C)	^{2}J(Pt–C)	$\bar{\nu}(^{13}C-O)$ [b]	$\bar{\nu}$(C–O) [b]
trans-$[PtH(CO)(PEt_3)_2][BF_4]$	182·8	990	7·5	1 958	2 043
trans-$[Pt(ClC_6H_4)(CO)(PEt_3)_2][BF_4]$	176·8	978	9	2 055	2 149
trans-$[Pt(CH_2Ph)(CO)(PEt_3)_2][BF_4]$	175·7	960	10	2 041	2 041
trans-$[Pt(NCS)(CO)(PPh_3)_2][BF_4]$	164·9 [c]	1 817	10	2 070	2 120
trans-$[Pt(NO_3)(CO)(PPh_3)_2][BF_4]$	160·5 [c]	1 817	10	2 069	2 130
	158·8	1 795	10		
trans-$[PtBr(CO)(PPh_3)_2][BF_4]$	159·0	1 772	9	2 065	2 111
trans-$[PtCl(CO)(AsEt_3)_2][BF_4]$	158·8	1 740		2 059	2 104
trans-$[PtCl(CO)(PPh_3)_2][BF_4]$	158·6	1 788	9	2 074	2 120
trans-$[PtCl(CO)(AsPh_3)_2][BF_4]$	158·2	1 724		2 063	2 138
trans-$[PtI(CO)(PPh_3)_2][BF_4]$	157·4	1 658	6	2 051	2 120
cis-$[PtCl_2(CO)(AsEt_3)]$	155·8	1 725		2 054	2 111
$[Hpy][PtCl_3(CO)]$	151·8	1 730		2 061	2 106
$[PtBr(CO_2Me)(PPh_3)_2]$	169·3	1 345	7·5	1 602	1 637
$[PtCl(CO_2Me)(PPh_3)_2]$	168·5	1 346	7·5	1 600	1 637
$[PtCl_2(CNMe)(AsEt_3)]$	107·2 [d]	1 723			

[a] For solutions in $CDCl_3$ (unless otherwise stated) relative to $SiMe_4$ as internal standard. [b] For solutions in $CHCl_3$. [c] For solutions in $(CD_3)_2CO$. [d] Refers to CH_3NC; $\delta(CH_3NC)$ 31·8 p.p.m.

Platinum(II) forms a wide range of carbonyl species. Neutral, cationic, and anionic complexes are known and present a particularly useful system for studies of the metal–carbonyl bond. We now report ^{13}C n.m.r. data for the series of anionic, neutral, and cationic derivatives *trans*-[PtX(CO)L,L′] (X = anionic *trans*-ligand and L,L′ = anionic or neutral *cis*-ligands) in which the incorporation of ^{13}CO has greatly augmented the signal to noise ratio of both the central carbonyl absorption and its accompanying satellites ($I = 1/2$ for ^{195}Pt in 33% abundance). Accurate chemical-shift and coupling-constant information has been obtained with short accumulation times for relatively small samples in the presence of a shiftless relaxation reagent, $Cr(pd)_3$ (pd = pentane-2,4-dionate). All such ^{13}CO species are analogues of reported[3] unlabelled derivatives and show the expected decrease in i.r. carbonyl-stretching frequency consistent with isotopic substitution (Table).

RESULTS AND DISCUSSION

The nature of the metal–ligand bond in a molecule depends on many factors. For platinum(II) derivatives there is a considerable body of evidence available on the relative directing effects in substitution reactions of groups *trans* to the leaving group (*trans*-effect series). This kinetic lability has been correlated with both σ- and π-components of the platinum–ligand bonds within the complex. In contrast, the *trans*-influence series has been correlated with the effect of the *trans*-ligand on ground-state properties of the molecule (as opposed to activated-state properties of the *trans*-effect) and has been discussed recently in terms of variation in bond-length data in platinum(II) complexes. The *trans*-influence series has been mainly attributed to variation in the σ-bonding network and in particular to variation in the degree of ‘ *s* ’ character in a metal–ligand bond on varying the nature of the group (*trans* to the ligand).

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[1] M. H. Chisholm, H. C. Clark, L. E. Manzer, J. B. Stothers, and J. E. H. Ward, *J. Amer. Chem. Soc.*, 1973, **95**, 8574.

[2] H. C. Clark and J. E. H. Ward, *J. Amer. Chem. Soc.*, 1974, **96**, 1741.

[3] W. J. Cherwinski and H. C. Clark, *Inorg. Chem.*, 1971, **10**, 2263.

N.m.r. coupling-constant data, notably $^1J(^{195}Pt-^{31}P)$, $^2J(^{195}Pt-C-H^1)$, and $^1J(^{195}Pt-^{13}C)$ in a series of platinum derivatives, have recently been utilised as an indication of the relative *trans*-influence for various ligand groups. In particular Clark and his co-workers [1] have arrived at *trans*-influence series by a consideration of the variation in magnitude of $^1J(^{195}Pt-^{13}C)$ in a group of platinum-methyl complexes. Their work assumes that the magnitudes of the coupling constants are dominated by the Fermi-contact contribution which in turn is related to the platinum 6*s*-orbital contribution to the Pt–L bond (see below). Within such a series it has been suggested that bonds to platinum gain in '*s*' and '*d*' character at the expense of '*p*' for an increase in σ-donor properties of the ligands; this leads to the converse effect for the Pt–L bond in the *trans*-position, so that a decrease in $^1J(^{195}Pt-^{13}C)$ coupling is taken to indicate an increase in the '*s*' character in the *trans*-bond and higher *trans*-influence of the group under consideration.

Applying the theory of Pople and Santry for coupling in a bond A–B, the coupling constant $^1J(^{195}Pt-^{13}C)$ is expressed by relation (1) where $\alpha_A{}^2$ is the '*s*' character

$$^1J(^{195}Pt-^{13}C) \propto \frac{\alpha_{Pt}{}^2\alpha_C{}^2}{^3\Delta E}|\psi Pt(6s)(0)|^2|\psi C(2s)(0)|^2 \quad (1)$$

of the hybrid used by A in the bond A–B, $|\psi(0)|^2$ the electron density of the orbital evaluated at the nucleus, and $^3\Delta E$ the mean triplet-excitation energy. In applying this relation it has normally been assumed that the energy separation, $^3\Delta E$, is reasonably constant for the series considered, and the main contribution to the variation in the coupling constant is associated with changes in '*s*'-orbital contribution from either the ligand or the metal hybrid orbital used in the bonding. This in turn has been related to the variation in the '*p*'-electron contribution to the bonds as indicated above. For planar platinum(II) derivatives, however, the *s* and d_{z^2} orbitals of the metal have the same symmetry and may therefore be mixed in any hybrid-orbital scheme considered. The relative contribution of these two orbitals to the bonding orbital will depend on the energy separation of the two orbitals, the orbital energy of the combining ligand orbitals, and the degree of overlap between the appropriate orbitals. A variation in the coupling constant may therefore reflect this change in the relative d_{z^2}–*s*-orbital contribution rather than reflect the variation in the '*p*'-orbital component of the bond *trans* to the bond as discussed above.

Since the coupling constant $^1J(^{195}Pt-^{13}C)$ is large for platinum–carbonyl complexes (*ca.* 1 800 Hz), its dependence on ligand groups seemed a useful method of assessing the *trans*-influence series. In the Table we report data for a range of complexes. The coupling constants for the platinum–carbonyl group fall into two ranges; within each range the variation is comparatively small. For ligands with a relatively low *trans*-influence the coupling constants are in the range 1 658—1 817 Hz, increasing gradually with decreasing *trans*-influence in the series I > Br > Cl > NO_3. The position of the thiocyanate ion in this series is of interest since the very high value of the coupling constant, *J* 1 817 Hz, implies a relatively low position in the *trans*-influence series. This contrasts markedly to its position in the '*trans*-effect' series where it is about equal to that of the iodide ion or phenyl group. However, the situation is complicated by the use of different solvents in these measurements and certainly for the nitrate complex a small but significant solvent effect was observed. A similar anomaly was noted by McWeeny *et al.*[4] for the positions of ethylene and carbon monoxide which occur with a high '*trans*-effect' but low '*trans*-influence' in the two respective series. The large coupling constant here may be correlated with the increase in the Pt–C σ-bond strength induced by the π-bonding capacity of the thiocyanate ligand, although it must be emphasised that small changes in the coupling constants may relate to factors other than changes in '*trans*-influence.' For ligands with a high *trans*-influence a large change was observed in the coupling constant (*J* 960—990 Hz), which is consistent with the above interpretation. Although there appear to be two distinct groups, the range of complexes studied do not really allow for a detailed consideration of the variation within each group. The very large change in coupling constant between the two groups, however, does reflect the anticipated variation in the '*s*'-orbital contribution between the ligand types. This variation may in part reflect the very high ligand-field strength of the hydrido- and carbon-bonded groups since this would be associated with a large value of the $^3\Delta E$ separation and a concomitant smaller value of the coupling constant from the Pople–Santry equation.

The chemical-shift data obtained for the co-ordinated carbonyl group also reflect the two groups of coupling constants observed. For the derivatives in which small coupling constants are found the chemical-shift values approached the value of free carbon monoxide (180·5 p.p.m.) indicating a very pronounced effect on the nature of the Pt–CO bonds by the *trans*-group. In agreement, the *X*-ray structure [5] of the two cations *trans*-$[Pt(X)(CO)(PEt_3)_2]^+$ (X = Cl and *p*-ClC_6H_4) show large changes in the Pt–C–O bond lengths with variation in the group X. Thus the Pt–C bond length changes from 1·78 Å in the chloride to 1·967 Å in the aryl derivative, the related bond lengths of the CO group being 1·14 and 1·063 Å respectively. The Pt–Cl bond length in the molecule where X = Cl was reported as 2·30 Å; this places the carbonyl group low in the *trans*-influence series (approximately at the position of chloride ion).

For a given *trans*-ligand, X = Cl, both $^1J(^{195}Pt-^{13}C)$ and the chemical shifts were relatively insensitive to changes in the nature of the *cis*-ligands L and L′. These observations are consistent with the proposed decrease in importance of the *cis*-influence. As the

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[4] R. McWeeny, R. Mason, and A. D. C. Towl, *Discuss. Faraday Soc.*, 1969, **47**, 20.

[5] J. S. Field and P. J. Wheatley, *J.C.S. Dalton*, 1974, 702.

charge on the platinum derivatives was varied from negative to neutral to positive, a small downfield shift in the carbonyl resonance was observed with increasing negative charge. However, the magnitude of platinum coupling to co-ordinated carbon monoxide remained essentially constant for the related derivatives, *i.e.* $[PtCl_3(CO)]^-$, *cis*-$[PtCl_2(CO)(AsEt_3)]$, and *trans*-$[PtCl(CO)(AsEt_3)_2]^+$.

A slight decrease in the value of the CO frequency was observed on varying the charge on the complex. A variation of 4 cm^{-1} on changing from the neutral *cis*-$[PtCl_2(CO)(AsEt_3)]$ to the anionic complex $[Pt(CO)Cl_3]^-$, however, is very much smaller than would normally be anticipated. The variation within the series of cationic species does not follow the same order as the variation in coupling constants or chemical shift, the hydrido- and carbon-ligand (other than CO) species spanning the two extremes of the range observed. However, in the case of the hydrido-group this comparison is suspect as there will be significant interaction between the platinum–hydrogen and –carbonyl vibrations in this molecule. Even so these results are in conflict with those of Clark and his co-workers [1] and others who have suggested that ^{13}C shieldings are linearly related to ν(CO).

The ready preparation of the alkoxocarbonyl derivatives from the carbonyls allowed us to investigate the variation in the coupling constant $^1J(^{195}Pt-^{13}C)$ with change in hybridisation of the platinum-bound carbon ($sp \rightarrow sp^2$). The complex *trans*-$[PtCl(CO)(PPh_3)_2]^+$ reacted readily with methanol to yield the labelled neutral alkoxocarbonyl derivative *trans*-$[PtCl(CO_2Me)(PPh_3)_2]$. This change to an approximately sp^2 state at bound carbon was accompanied by an upfield shift in the position of the carbonyl resonance and a pronounced decrease in coupling to platinum from 1 788 to 1 346 Hz. This latter observation is consistent with the lower proportion of *s* character in the carbon σ-bonding orbital formed after rehybridisation and agrees with the observed orders ($sp > sp^2 > sp^3$) for $^1J(^{195}Pt-^{13}C)$ in other cationic platinum(II) derivatives and $^1J(^{13}C-^1H)$ for hydrocarbons. Farnell *et al.*[6] also noted higher chemical shifts for carboxyl carbon compared to terminal carbonyl groups in the iron complex $[Fe(cp)(CO)_2(COMe)]$ (cp = η-cyclopentadienyl).

The effect on J of hybridisation at σ-bound carbon is further suggested by nearly identical values for the coupling constant from the metal to an L group ($\sim sp$) carbon in the neutral derivatives *cis*-$[PtCl_2L(AsEt_3)]$ (L = CO and CNMe) (J = 1 725 and 1 723 Hz respectively). The electronic distribution around the metal appears to be the same in both cases as the platinum coupling to CH_2 carbons of co-ordinated triethylarsine was similar (J 45 and 40 Hz). Clark and his co-workers ascribed similar results for $^1J(^{195}Pt-^{13}C)$ for the methyl–platinum group in the analogous cationic derivatives *trans*-$[PtMe(L)(AsMe_3)_2]^+$ to the similar *trans*-influence of L = CO and CNMe (J 470 and 476 Hz). Although platinum coupling to the carbonyl group was observed, a comparison with $^1J(Pt-L)$ for the isocyanide derivative was not possible since, for the complex *trans*-$[PtMe(CNMe)(AsMe_3)_2]^+$ isocyanide carbon could not be detected at the probe temperatures employed. These workers suggested interference from ligand-exchange processes and severe signal broadening due to the ^{14}N nuclear spin. However, since at −70 °C both effects are somewhat offset by the viscosity of the solution, we successfully observed both the central isocyanide-carbon resonance and its weaker accompanying side bands arising from coupling with platinum after long periods of spectral accumulation. Previously only Farnell *et al.*[6] have reported the ^{13}C n.m.r. chemical shift (147·4 p.p.m.) of isocyanide carbon in an organometallic complex with iron; for organic isocyanides, δ is 157—169 p.p.m.

EXPERIMENTAL

All ^{13}CO complexes used in this study were prepared by established methods employing ^{13}CO in place of ^{12}CO. The amount of ^{13}CO incorporation was established by an i.r. method. All reactions and recrystallisations were carried out using spectroscopic-grade solvents. Microanalyses were by the Analytical Laboratory of this department. The i.r. spectra were recorded on a Perkin-Elmer 621 spectrometer using 0·5 mm sodium chloride cells. ^{13}C N.m.r. spectra were obtained on a Varian Associates XL 100 spectrometer operating in the transform mode at 25·2 MHz, employing solvent-deuterium lock. Shifts were measured in p.p.m. from tetramethylsilane.

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[6] L. R. Farnell, E. W. Randall, and E. Rosenberg, *Chem. Comm.*, 1971, 1078.