Carbene Complexes. Part III. Carbon-13 Nuclear Magnetic Resonance Studies of Carbene Complexes of 1,3-Diorganoimidazolidin-2-ylidenes

By **David J. Cardin, Bekir Çetinkaya, Engin Çetinkaya,** and **Micheal F. Lappert,** School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ

Edward W. Randall * and **Edward Rosenberg,** Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS

^{13}C N.m.r. data for the series of *cis*- and *trans*-neutral carbene complexes $[MX_2(R_3'E)(\overline{\text{CNRCH}_2\text{CH}_2\text{N}}\text{R})]$ (where M = Pt, Pd; E = P, As; X = Cl, Br, Me; R = Me, Ph; and R' = Et, Pr^n, Bu^n), and the related complexes $\text{Fe(CO)}_4\overline{\text{CN(CH}_3)\text{CH}_2\text{CH}_2\text{N}}(\text{CH}_3)$ and *cis*-$\text{Cr(CO)}_4[\text{C(SCH}_3)_2]_2$ are presented. The chemical shift of the carbene carbon is sensitive to the *trans*-ligand. Unusual long range ^{31}P–^{13}C couplings to the ring methylene carbon and ^{195}Pt–^{13}C$_{\text{carb}}$ couplings are reported for four of the complexes studied.

THE present work results from complementary studies in two laboratories. At Sussex, a series of neutral *cis*- and *trans*-Pt^{II} and Pd^{II} complexes has been prepared,[1,2] and the *trans*-influence of the carbene ligand assessed as approximately equal to R_3P on the basis of i.r., ^{1}H and ^{31}P n.m.r.,[3] and *X*-ray[4] data. Some related Cr^0 and Fe^0 complexes have also been obtained.[5] At Queen Mary College, ^{13}C n.m.r. spectra of a wide range of organic and organometallic compounds have been examined,[6] including a series of octahedral carbene complexes of Cr^0 and W^0;[7] noteworthy is the large downfield shift characteristic of the carbene carbon atom and the influence of the *trans*-ligand on this shift. ^{13}C N.m.r. data have now been collected at Queen Mary College on the Sussex compounds (I)—(XVI), as summarised in Tables 1—3, and their significance is discussed below.

Compounds (I)—(XVI) include a number of *cis–trans*-isomeric pairs. As has been observed,[1,4] *cis*-complexes are less soluble than *trans*-isomers, possibly because of their greater ionicity which is consequent upon the *trans*-influence order: carbene > Cl$^-$ or Br$^-$. To obtain *cis*-compounds of adequate solubility to permit the recording of ^{13}C n.m.r. spectra, we used *N*-methyl- rather than *N*-phenyl-carbenes, or tributyl- rather than triethyl-phosphine. The arsine complexes were chosen so that for corresponding phosphine derivatives there was no ambiguity in assignment between separations due to chemical shifts and coupling involving ^{31}P.

Carbene Carbon Chemical Shifts (δC_{carb}).—The observed chemical shift range for δC_{carb} in the series $M(CO)_5C(X)(Y)$ (where M = Cr or W; X = OR, O$^-$, NR$_2$, or SR; and Y = alkyl or aryl) is 250—360 p.p.m. downfield from Me$_4$Si,[7] whereas the range for the series studied here is to higher fields at 175—215 p.p.m. This overall shift in the range for the present series is probably due in part to the presence of *two* hetero-atoms bound to the carbene carbon, which increases the local π-density, causing an upfield shift.[7,8] However, δC_{carb} for $[Pt(CH_3)_2As(CH_3)_3\text{-}C(OCH_3)CH_3]^+PF_6^-$ (321 p.p.m.)[9] which has a mono-hetero function, is 40 p.p.m. to high field of δC_{carb} in $Cr(CO)_5C(OCH_3)CH_3$ (362 p.p.m.)[7] and 10 p.p.m. to high

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field of δC_{carb} in $W(CO)_5C(OCH_3)CH_3$.[1] It has been suggested for sp^2 carbons that mixing of $2p$ carbon orbitals with empty metal d-orbitals in the magnetic field produces a low field shift (σ_p at carbon due to the metal is negative).[10] This effect would be expected to be smaller for the more occupied d^8-square planar complexes than for the d^6-octahedral complexes as has been suggested for protons bound to a transition metal.[11]

The smaller value of δC_{carb} in (XVI) relative to other chromium carbene complexes can also be explained by the presence of two lone pair donors bound to the carbene carbon. But here, chemical shift anisotropy of the sp^2 carbon (which may be small) is related to the overall geometry of the complex. There are three possible relative orientations of the $2p$-orbitals on each carbene carbon in (XVI) with respect to the magnetic field (both $\|$; both $\perp^r$; and one $\|$, one $\perp^r$). The configuration with one orbital $\|$ and one $\perp^r$ to the magnetic field would tend to average the large anisotropy associated with sp^2 carbons bound to transition metals[8] thus causing an upfield shift.

TABLE 1

^{13}C Chemical shifts [a] and coupling constants [b] of 1,3-diorganoimidazolidin-2-ylidene carbene complexes

No.	Compound	δC_{carb}	$^2J(C\text{—}M\text{—}^{31}P)$	δCH_2 ring	$^4J(^{13}C\text{—}^{31}P)$	$^3J(^{13}C\text{—}^{195}Pt)$
(I)	*trans*-$\mathrm{Cl_2Bu^n{}_3PPdL'}$ [c]	200·5	180·5	52·3	7·3	
(II)	*cis*-$\mathrm{Cl_2Bu^n{}_3PPdL}$ [c]	195·1	<2·4	52·1	<2·4	
(III)	*trans*-$\mathrm{Cl_2Et_3AsPtL}$ [c,f]	188·6		51·7		14·6
(IV)	*cis*-$\mathrm{Cl_2Et_3AsPtL}$ [c,g]	175·1		51·2		58·6
(V)	*trans*-$\mathrm{Cl_2Et_3PPtL}$ [c]	197·3	156·2	52·3	7·3	29·2
(VI)	*cis*-$\mathrm{Cl_2Et_3PPtL}$ [c]	177·8	*ca.* 50	51·9	<2·4	43·8
(VII)	*trans*-$\mathrm{Cl_2Pr^n{}_3PPtL}$ [c]	195·8	151·2	52·2	6·0	28·8
(VIII)	*cis*-$\mathrm{Cl_2Pr^n{}_3PPtL}$ [c]	178·0	7·2	51·9	<2·4	48·0
(IX)	*trans*-$\mathrm{Cl_2Bu^n{}_3PPtL}$ [c]	196·5	146·4	52·6	7·9	34·2
(X)	*cis*-$\mathrm{Cl_2Bu^n{}_3PPtL}$ [c]	178·0	*ca.* 60	52·3	<2·4	43·8
(XI)	*trans*-$\mathrm{Br_2Et_3PPtL}$ [c]	196·2	148·8	52·8	7·3	29·2
(XII)	*trans*-$\mathrm{Cl_2Et_3PPtL'}$ [c]	192·7	170·6	52·2	4·9	39·0
(XIII)	*trans*-$\mathrm{Me_2Et_3PPtL}$ [d,h]	218·1	144·0	49·6		
(XIV)	*cis*-$\mathrm{Me_2Et_3PPtL}$ [d,i,l]	214·5	14·4	51·3		24·4
(XV)	$\mathrm{(CO)_4FeL}$ [d,j]	213·2		51·6		
(XVI)	*cis*-$\mathrm{(CO)_4Cr[C(SCH_3)_2]_2}$ [d,k]	141·6				

[a] ±0·1 P.p.m. downfield (positive) with respect to internal tetramethylsilane. [b] ±2·4 Hz. [c] Run in 75% $CDCl_3$ + 20% C_6F_6 + 5% tetramethylsilane. [d] Run in 75% C_6F_6 + 20% C_6F_6 + 5% tetramethylsilane. [e] Run in 75% $(CD_3)_2CO$ + 20% C_6F_6 + 5% tetramethylsilane. [f] $^1J(^{195}Pt\text{—}^{13}C)$ 1073·6 Hz. Data not available for all compounds owing to lack of solubility. [g] $^1J(^{195}Pt\text{—}^{13}C)$ 756·4 Hz. [h] $\delta CH_3 = -16{\cdot}6$ p.p.m, $^2J(^{31}P\text{—}^{13}C)$ 9·8 Hz. [i] CH_3 (*trans-*) = +11·9 p.p.m., $J(^{31}P\text{—}^{13}C)$ <2·4 Hz, CH_3(*cis-*) = −18·9 p.p.m., $J(^{31}P\text{—}^{13}C)$ = 12·2 Hz (*trans*-relative to carbene ligand). [j] δCO 217·4 p.p.m. [k] δCO(*cis-*) = 215·9 p.p.m., δCO(*trans-*) = 277·0 p.p.m., δCH_3 17·7, 29·5 p.p.m. [l] $J(^{195}Pt\text{—}^{13}C)$ = 570 Hz. $\mathrm{L = \overline{C{\cdot}NMe{\cdot}[CH_2]_2{\cdot}N}Me,\ L' = \overline{C{\cdot}NPh{\cdot}[CH_2]_2{\cdot}N}Ph}$.

TABLE 2

Chemical shifts [a] and coupling constants [b] of 1,3-alkyl and aryl groups in 1,3-disubstituted imidazolidin-2-ylidenecarbene complexes

No.	R	C(1)	$^3J(^{13}C\text{—}^{195}Pt)$	C(2,6)	C(3,5)	C(4)
(I)	Ph	143·1		125·2	130·1	127·6
(II)	Me	37·9				
(III)	Me	36·6	24·4			
(IV)	Me	37·2	43·9			
(V)	Me	37·4	24·4			
(VI)	Me	38·0	43·8			
(VII)	Me	36·4	24·0			
(VIII)	Me	37·8	40·8			
(IX)	Me	36·7	24·2			
(X)	Me	38·2	43·8			
(XI)	Me	37·1	24·4			
(XII)	Ph	142·2		124·8	129·2	126·9
(XIII)	Me	36·4	24·4			
(XIV)	Me	36·2	48·8			
(XV)	Me	39·2				

[a] ±0·1 P.p.m. downfield (positive) with respect to internal tetramethylsilane. [b] ±2·4 Hz.

The range of δC_{carb} observed in these compounds is 51 p.p.m. for the *trans*-series and 29 p.p.m. for the *cis*-series. Furthermore, the carbene carbon atom becomes more deshielded the greater the *trans*-influence of the group *trans*- to δC_{carb} in the complex. Thus for the compounds $\mathrm{L_2(Et_3P)Pt\overline{C{\cdot}NMe{\cdot}CH_2{\cdot}CH_2{\cdot}N}Me}$ (L = Cl or Me), we have in (VI) (C_{carb} *trans* to Cl)δC_{carb} = 177·8 p.p.m.; in (V), (C_{carb} *trans* to Et_3P)δC_{carb} = 197·3 p.p.m.; and in (XIV), (C_{carb} *trans* to Me), δC_{carb} = 214·5 p.p.m., following the order of increasing *trans*-influence. Similarly replacement of Et_3As in complex (III) (δC_{carb} = 188·6 p.p.m.) by Et_3P in (V) (δC_{carb} = 197·3) follows this order. However, with the strong ligand field influence of the methyl group both *cis*- and *trans*-isomers have highly deshielded C_{carb}, presumably reflecting a *cis* influence as well. Shifts of proton resonances to lower field have also been observed with increasing ligand-field strength of the *trans*-ligand in platinum hydrides.[12]

The large difference in δC_{carb} between *cis*- and *trans*-isomers may be related to differences in anisotropies at the metal atom or to differences in the effective ΔE at the carbene as a consequence of variations in (p–d) π-bonding[7] with different *trans*-ligands.

The upfield shift [17 p.p.m. in (VIII) with respect to (II)] of the carbene carbon produced by replacement of Pd by Pt is reminiscent of the similar shift (10—15 p.p.m.) produced by replacement of a lighter by a

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[11] A. P. Ginsburg, *Transition Metal Chem.*, 1966, **2**, 111.

[12] A. D. Buckingham and P. J. Stephens, *J. Chem. Soc.*, 1964, 4583.

heavier transition metal in the same group in the case of Cr, Mo, and W, carbene [7] and carbonyl [8] complexes.

It is difficult to compare the value of δC_{carb} in complex (XV) meaningfully with the values for the rest of the series because of variations in the other ligands and in geometry. A shift to low field would be expected, however, for a first row transition metal [7] as is observed. The value of δCO in (XV) (217·4 p.p.m.) compared with $Fe(CO)_4PR_3$ (215 p.p.m.) suggests that the imidazolidinylidene ligand is a charge donor comparable with PR_3.[7]

The chemical shifts for the other carbons in the imidazolidinylidene ligand are given in Tables 1 and 2. These shifts are typical for hydrocarbons bound to nitrogen [13] and will not be discussed further.

TABLE 3

^{13}C Chemical shifts [a] and coupling constants [b] of tertiary phosphines ($R_3'P$) in 1,3-dialkylimidazolidin-2-ylidene carbene complexes

No.	R′	C(1)	$^1J(^{13}C-^{31}P)$	$^2J(^{13}C-^{195}Pt)$	C(2)	$^2J(^{13}C-^{31}P)$	C(3)	$^3J(^{13}C-^{31}P)$	C(4)
(I)	Bu^n	24·1	14·6		26·8	<2·4	21·4	24·4	14·1
(II)	Bu^n	28·8	12·2		26·4	<2·4	21·7	4·9	12·7
(III)	Et	14·5		34·1	11·3				
(IV)	Et	9·3		24·4	1·0				
(V)	Et	16·0	36·6	24·4	8·4	<2·4			
(VI)	Et	16·3	39·0	43·8	8·3	<2·4			
(VII)	Pr^n	23·1	31·2	24·4	17·9	<2·4	16·1	13·2	
(VIII)	Pr^n	26·5	36·0	48·0	18·0	<2·4	16·0	15·6	
(IX)	Bu^n	25·2	12·2		26·9	<2·4	22·6 20·3	14·6 14·6	14·4
(X)	Bu^n	24·9	12·2	34·4	27·1	<2·4			14·1
(XI)	Et	14·4	36·6	24·4	8·1	<2·4			
(XII)	Et	12·6	31·7		7·5	<2·4			
(XIII)	Et	14·9	28·8		8·4	<2·4			
(XIV)	Et	17·3	24·4	24·4	8·5	<2·4			
(XV)	Et	17·7	[c]			3·6 [d] 8·4			

[a] ±0·1 P.p.m. downfield with respect to internal tetramethylsilane. ±2·4 Hz. [c] Observed as six lines; separations: 3·6, 38·4, 3·6, 32·4, 32·4, ±1—2 Hz. [d] Observed as a doublet of doublets.

^{13}C *Coupling Constants*.—The magnitudes of the $^1J(^{13}C_{carb}-^{195}Pt)$ decrease in the order (III) > (IV) > (XIV). This is not in agreement with the idea that $^1J(^{195}Pt-^{13}C$ metal) [2] is inversely related to charge donor ability of the *trans*-ligand.[9] Assuming a dominant Fermi contact term, this result may still reflect changes in the hybridisation of the Pt–C$_{carb}$ bond. Thus the platinum atom directs more of its *s*-density towards the more electropositive phosphine, arsine, or methyl group than towards chlorine which increases the *s*-character in the mutually shared sigma bonding orbitals.

The two- and three-bond platinum couplings to the carbons in the phosphine, arsine, and carbene ligands (Tables 1—3) are all very similar in magnitude within the series. It is interesting to note, however, that these couplings are always larger in the *cis*- than in the *trans*-isomers.

The most prominent trend in the phosphorus–carbene couplings is that $|^2J|(trans\text{-}) \gg |^2J|\ (cis\text{-})$ as has been found for $^2J(^{31}P-M-^{31}P)$ [14] and $^2J(^{31}P-M-^{13}CO)$.[15] The carbene resonances in the *cis*-isomers were considerably broadened (perhaps due to a smaller electric field gradient at the nitrogen in the *cis*-cases) which made accurate evaluation of $^2J(^{31}P-M-^{13}C)$ difficult in (VI) and (X) (see Table 1).

The magnitudes of $^2J[^{31}P-C(2)]$ in the phosphine ethyl and propyl groups is reduced to <2·4 Hz, compared with values of 13—15 Hz in the free ligands.[16] This has also been observed in $(n\text{-}C_4H_9)_3P$ in octahedral phosphine complexes.[15] We have used these facts to assign the lowest field resonance in the $(n\text{-}C_4H_9)_3P$ complexes to the C(2) carbons. This represents a departure from the normal order of shifts [*viz.*, C(1) > C(2) > C(3) > C(4)] in the free ligand and in the octahedral complexes.[15,16] Indeed, the C(1) resonances in the $(n\text{-}C_3H_7)_3P$ and Et_3P groups are also found to slightly higher fields than in the free ligands, in contrast with the shifts in octahedral complexes.

The CH_2 carbon of the imidazolidine ring was observed as a doublet resonance with separation of 4·9—7·3 Hz for all the *trans*-isomers. A singlet resonance was observed for this carbon in the *cis*-isomers. We tentatively assign this splitting to a long range phosphorus–carbon coupling which is consistent with other $^nJ(^{31}P-^{13}C)$ values.[16] We also observe long range couplings of the hydrogen atoms of the ring methylene groups with ^{195}Pt nuclei in the ^{1}H n.m.r. spectra (see Part IV of this series),[3] and the chemical shifts of these protons are sensitive to substituents on the nitrogen atom of the *other* ring in the nitrate salts derived from the bis-(imidazolidinylidenes) (olefins).

An apparently anomalous phenomenon was observed for the C(3) carbons of the butyl groups in (IX) and (X): a doublet of doublets is observed for the *trans*-isomer and a broad hump in the region expected for this resonance in the *cis*-isomer. We can offer no

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[16] B. E. Mann, *J.C.S. Perkin II*, 1972, 30.

convincing explanation for these observations at this time.

Conclusions.—From these studies four noteworthy trends emerge: (*a*) The higher field chemical shifts observed for the carbene complexes studied here compared with those previously examined by ^{13}C n.m.r.,[6,7] can be ascribed to greater π-electron density at the carbene carbon caused by two directly bound nitrogen atoms and to decreased paramagnetic shielding by the metal atom expected for d^8 square planar complexes. It is not possible now to weigh these two factors, but the results for octahedral complexes of chromium suggest that the former is the dominant effect.

(*b*) The ^{13}C chemical shifts of the carbene complexes so far examined lie some 175—360 p.p.m. downfield from the tetramethylsilane. Such unique values, some of which parallel those of carbonium ions, will probably have considerable diagnostic value in carbene chemistry. In the present series we note that C_{carb} becomes more deshielded as the *trans*-influence of the group *trans* to the carbene increases. It should be noted, however, that the organometallic compounds with chemical shifts closest to those of C_{carb} include metal acyl compounds, which also have a metal bonded sp^2 carbon atom.

(*c*) There is a marked contrast in $^3J(^{13}C-^{195}Pt)$ coupling constants between the *cis* ($\leqslant 60$ Hz) and *trans* ($\geqslant 140$ Hz) complexes, a fact which could be used for assignment of stereochemistry, much as the well known $^1J(^{31}P-^{195}Pt)$ method.

(*d*) $^1J(^{31}P-C_{carb})$ does not follow the expected order based on the *trans*-influence of appropriate ligands. Instead, we believe that hybridisation effects at the platinum atom may be important, but the data as yet are insufficient to draw firm conclusions on this point.

EXPERIMENTAL

Spectra.—^{13}C Spectra were obtained on a Bruker HFX 13 spectrometer operating in the Fourier transform mode at 22·63 MHz. The ^{19}F resonance of C_6F_6 was used for locking purposes. Proton noise decoupling was accomplished with a 90 MHz broad-band decoupler. Spectral assignments in the hydrocarbon region were made with the use of off-centre double resonance experiments and known substituent parameters.

Solutions were prepared in *ca.* 50% w/v concentrations in deuteriated solvents. Solutions of (XV) and (XVI) were prepared in an inert atmosphere and run in 10 mm tubes under argon atmosphere.

Materials.—Compounds were prepared as described in ref. 2, or are to be published.[5]

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