Carbon Nuclear Magnetic Resonance Study of Rhodium–Olefin Complexes

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Summary The magnitude of the ^{103}Rh–^{13}C coupling constant and the substantial upfield shift of the olefinic carbon resonance upon complexation suggest that there is considerable s-character in olefin–rhodium bonds.

To investigate the mode of bonding of olefins to transition metals we have examined the ^{13}C n.m.r. spectra of a series of rhodium–olefin complexes. ^{13}C N.m.r. spectra at natural abundance were obtained using a spectrometer described previously.[1] Table 1 shows the spectral data for the olefin carbon atoms of the rhodium complexes studied. ^{103}Rh–^{13}C Coupling of ca. 14—16 Hz, and substantial upfield shift of the olefinic resonance upon complexation are shown. The coupling constant appears small. When the small gyromagnetic ratio of ^{103}Rh is accounted for, the reduced

coupling constant, $K(^{103}$Rh–^{13}C$')$ is ca. $3 \times K(^{13}$C–^{1}H$)$. Although electron–nuclear dipolar interactions can contribute to scalar coupling,[2] a Fermi contact interaction is still likely to be dominant since the reduced coupling constants are quite large. A study of (C_5H_5)Rh$(\sigma$-allyl)- $(\pi$-allyl), first prepared by Powell and Shaw,[3] shows a 26 Hz coupling for the rhodium–carbon σ-bond. Assuming sp^3-hybridization for the σ-allyl methylene carbon one can determine that the s-character, $\rho = 0.96$ J.† From this the s-character of the rhodium–olefin-carbon bond is estimated to be ca. 15%. One extreme view of olefin–metal bonding involves σ-bond formation of an sp^3-rehybridized olefin carbon and a dsp^2 metal orbital. Our estimate of 15% s-character implies a contribution from this bonding scheme of about 60%.‡

† We have assumed that the scaling of $J(^{103}$Rh–^{13}C$)$ is dominated by the s-character dependence of the Fermi contact term. $J(^{13}$C–H$)$ is dependent on a second portion of the Fermi contact term as well, namely the effective nuclear charge (Z^*).[4] At present we must assume this term is constant since its variance in these rhodium complexes is not known.

‡ Cook and Wan estimate 28% s-character in $(Ph_3P)_2$Pt(C_2H_4) and thus a 100% contribution from the σ-bonded scheme.[5]

The previously noted substantial upfield shift for the olefinic carbon resonance upon complexation ranges from *ca.* 50 to as large as 115 p.p.m. in the 2,3,5,6 positions of may be due to the fortuitous cancellation of factors in the coupling constant expression of equal magnitude but opposite sign, or it may be due to a difference in bonding of

TABLE 1

[13]C N.m.r. data for free and co-ordinated olefin carbon atoms

Compound				δc (p.p.m.)[a]	Δc[b] (p.p.m.)	$J([13]C–H)$ (Hz)[c]	$J([103]Rh–[13]C)$ (Hz)
cod[d]	..	..	..	65·0	—	150	—
C_2H_4	..	..	..	71·2[e]	—	—	—
nbd[d]	..	..	..	48·9	—	174	—
(cod)Rh(C_5H_5)	..	..	..	130·4	+65·4	152	14
(cod)Rh(acac)[d]	..	..	..	116·8	+51·8	156	14
(cod)Rh(acac-F_3)	..	..	..	116·5	+51·5	154	14
(cod)Rh(acac-F_6)	..	..	..	114·6	+49·6	152	16
(C_2H_4)$_2$Rh(C_5H_5)	..	..	..	132·8	+61·2	160	10
(C_2H_4)$_2$Rh(acac)	..	..	..	156·5	+85·3	158	14
(nbd)Rh(C_5H_5)	..	..	..	164·1	+115·2	176	10

[a] Chemical shifts relative to CS_2 = 0 p.p.m.
[b] Δc represents the shift upfield of the olefin resonance upon complexation.
[c] ± 5 Hz.
[d] cod = cyclo-octa-1,5-diene, nbd = norbornadiene, acac = acetylacetone.
[e] In CCl_4 solution (W. W. Conover, Indiana University).

norbornadiene.§ This resonance falls in the region where one would expect the resonances of saturated carbon atoms. The ^{13}C screening tensor has been shown to be dominated by the paramagnetic shielding term,[7] which is dependent on changes in the electron density, in the π-bond order, or in the average excitation energy,[8] (caused by the mixing of excited states into the ground state due to the perturbation of the magnetic field). The σ-bond model indicated above for olefin–metal bonding results in a substantial decrease in the π-bond order of the olefin upon complexation and leads to an upfield shift. An increase in s-character is known empirically to lead to an upfield shift of the resonance. The magnitude and effect of a change in average excitation energy from free to co-ordinated olefin is not yet known.

Table 2 gives the [13]C n.m.r. data for the cyclopentadienyl carbon atoms of the rhodium complexes studied. The chemical shift values are nearly constant and no [103]Rh–[13]C coupling is observed. The absence of [103]Rh–[13]C coupling

cyclopentadienyl and olefin ligands to a transition-metal atom. Thus it is possible that olefin-metal bonds have substantial σ-character while cyclopentadienyl–metal bonds have predominantly π-character.

TABLE 2

[13] C N.m.r. data for cyclopentadienyl carbon atoms

Compound			δc (p.p.m.)[a]	$J([13]C–H)$ (Hz)
(cod)Rh(C_5H_5)	..	..	106·3	167
(C_2H_4)$_2$Rh(C_5H_5)	..	..	105·9	174
(nbd)Rh(C_5H_5)	..	..	108·0	172
(CO)$_2$Rh(C_5H_5)	..	..	105·2	176

[a] Chemical shifts relative to CS_2 = 0 p.p.m.

§ A complexation shift of 4 p.p.m. for $AgNO_3$(olefin) complexes has been reported.[6]

[1] A. O. Clouse, D. Doddrell, S. B. Kahl, and L. J. Todd, *Chem. Comm.*, 1969, 729.
[2] N. F. Ramsey, *Phys. Rev.*, 1953, **91**, 303.
[3] J. Powell and B. L. Shaw, *J. Chem. Soc. (A)*, 1968, 583.
[4] D. M. Grant and W. Litchman, *J. Amer. Chem. Soc.*, 1965, **87**, 3994.
[5] C. D. Cook and K. Y. Wan, *J. Amer. Chem. Soc.*, 1970, **92**, 2595.
[6] R. G. Parker and J. D. Roberts, *J. Amer. Chem. Soc.*, 1970, **92**, 743.
[7] M. Karplus and J. A. Pople, *J. Chem. Phys.*, 1963, **38**, 2803.
[8] L. Salem, "The Molecular Orbital Theory of Conjugated Systems," Benjamin, New York, 1966, p. 221.