Evidence for a π-Donor Effect in Transition-metal Alkyls from H–D Coupling Constants

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POPLE and BOTHNER-BY have suggested that J_{H-H} in methyl and methylene derivatives may be interpreted in terms of the σ- and π-effects of the substituents.[1] We have determined J_{H-D} for some monodeuteriomethyl, CH_2D, and $-C_6H_4{\cdot}CH_2D$ derivatives of transition metals. The corresponding values of J_{H-H} for these compounds are given in the Table. The sign of J_{H-D} in the CH_2D group of the complex π-$C_5H_5Fe(CO)_2CH_2D$ has been determined by ^{13}C double resonance. This shows J_{H-D} to be opposite in sign to J_{C-H} and therefore to be negative. It is reasonable to assume this to be true for the sign of J_{H-D} for the other transition metal CH_2D complexes.

Values of J_{H-H} † *(calculated from observations on* J_{H-D}*).*

Compound	Solvent			
	MeCN	C_6H_6	C_6H_{12}	CS_2
π-$C_5H_5Ni(PPh_3)CH_2D$				$\mp 7{\cdot}9$
π-$C_5H_5Fe(CO)_2CH_2D$	$-8{\cdot}3$	$-8{\cdot}6$	$-8{\cdot}9$	$-9{\cdot}0$
π-$C_5H_5Mo(CO)_3CH_2D$	$\mp 8{\cdot}9$	$\mp 8{\cdot}8$		$\mp 9{\cdot}1$
$Mn(CO)_5CH_2D$		$\mp 9{\cdot}7$		$\mp 9{\cdot}8$
π-$C_5H_5W(CO)_3CH_2D$	$\mp 10{\cdot}0$	$\mp 10{\cdot}0$		$\mp 10{\cdot}2$
$BrHgCH_2D$		$\mp 10{\cdot}3$		$\mp 10{\cdot}3$
trans-$BrPt(PEt_3)_2CH_2D$	$\mp 10{\cdot}0$	$\mp 10{\cdot}4$	$\mp 10{\cdot}8$	
trans-$SCNPt(PEt_3)_2CH_2D$		$\mp 10{\cdot}2$		
trans-$NO_3Pt(PEt_3)_2CH_2D$		$\mp 10{\cdot}2$		
m-[π-$C_5H_5Ni(PPh_3)$]$C_6H_4{\cdot}CH_2D$				$\mp 12{\cdot}2$
p-[π-$C_5H_5Ni(PPh_3)$]$C_6H_4{\cdot}CH_2D$				$\mp 11{\cdot}9$
m-$BrC_6H_4{\cdot}CH_2D$		$\mp 13{\cdot}7$		
p-$BrC_6H_4{\cdot}CH_2D$		$\mp 14{\cdot}3$		

† All values ± 0·3 c./sec.

J_{H-H} is found to be solvent sensitive, changes as large as 0·8 c./sec. being observed. Such large solvent shifts are not found for saturated hydrocarbons though changes of 0·25 c./sec. are found for J_{ab} in $MeCHBr{\cdot}CH_aH_bBr$.[2] It seems likely that the solvent shifts found in this work arise from effects of solvent on the metal, for example co-ordination by the solvent.

Pople and Bothner-By considered the geminal coupling constants for methyl and methylene groups in terms of contributions from molecular orbitals formed from linear combinations of carbon hybrid-orbitals and hydrogen 1*s*-orbitals. The resulting orbitals have either σ- or π-symmetry. They showed that relative to methane (J_{H-H} $-12{\cdot}4$ c./sec.) an increase in J_{gem} could result from either electron withdrawal from the bonding σ-orbital or by electron donation to the bonding π-orbital. If the values for J_{H-H} of the transition metal methyl compounds are interpreted on this basis, in the cases of complexes where $|J|$ is rather less than 10, such as π-$C_5H_5Ni(PPh_3)CH_2D$, $|J_{H-H}|$ $7{\cdot}4 \pm 0{\cdot}3$ c./sec., one must conclude that either the metal is very electronegative (σ-pull) or there is a strong π-donor effect from the metal to the methyl group (or alternatively a combination of the two effects). Evidence from chemical shift data[3] suggests that the metal has a positive inductive effect in these low oxidation state carbonyl and π-cyclopentadienyl complexes and is electron donating rather than the reverse. Therefore we feel that the most reasonable explanation of the high J_{H-H} values is that there is a strong π-donor effect from the filled metal *d*-orbitals to the methyl group.

Independent support for this suggestion comes from the value for J_{H-D} in the *m*- and *p*-$CH_2D{\cdot}C_6H_4$-$NiPPh_3,\pi$-C_5H_5 complexes (Table). The values for the corresponding *m*- and *p*-$CH_2D{\cdot}C_6H_4Br$ are also given. The values for J_{H-H} in the nickel derivatives are greater than those of the bromo-compounds (assuming a negative sign) again indicating a metal π-donor effect. This is supported by the observation that the value for the *para*-compound is greater (or not less) than that for the *meta*-compound, π-donation being expected to be greater to the *para*- than to the *meta*-position, while withdrawal is expected to be less (*cf.* the values for the bromo-analogues).

It is possible that there may be direct interaction between the filled metal *d*-orbitals and the 1*s*-orbitals of the methyl hydrogens.[4] The Pople and Bothner-By treatment is only concerned with the relative contributions of the hydrogen orbitals to bonding and anti-bonding molecular orbitals and does not distinguish between effects caused by interaction of the metal with the carbon *p*-orbitals or with the hydrogen orbitals themselves. Indeed both mechanisms are likely to occur in transition metals.

Chemical support for the postulated strong π-donor properties of metals in these electron-rich complexes comes from the observation that π-$C_5H_5Fe(CO)_2CH_2Cl$ appears to react to form an intermediate carbene complex $[\pi$-$C_5H_5Fe(CO)_2$-$CH_2]^+$.[3,5]

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