ready been shown to react with several acidic borane intermediates.[14,15] One might have expected, then, that it might also react with the acid BH_3. It was our expectation that since no B_7 hydrides have been isolated, $B_6H_{10}\cdot BH_3$ might lose H_2 with formation of an acid[16] which would react with more B_6H_{10} to form a B_{13} hydride. This prediction appeared to be borne out when $B_{13}H_{19}$ was isolated by pyrolysis of B_6H_{10} in the presence of B_2H_6. However, the yield of $B_{13}H_{19}$ did not appear to be greatly affected when B_2H_6 was not added to the B_6H_{10}. Because of the low yields, no quantitative data were obtained to compare the two reactions accurately. Isolation of B_8H_{12}, its decomposition product $(B_{16}H_{20})$,[15] and its reaction products with B_2H_6 (n-B_9H_{15} and $B_{10}H_{14}$)[17] suggested the possibility that B_8H_{12} might be an intermediate in the formation of $B_{13}H_{19}$. There is also a structural similarity between B_8H_{12} and the larger of the two boron frameworks in $B_{13}H_{19}$. Loss of BH_3 from the known adduct of B_6H_{10} and B_8H_{12} $(B_{14}H_{22})$[15] might appear to be a suitable pathway for the formation of $B_{13}H_{19}$. Although no $B_{13}H_{19}$ was isolated when B_8H_{12} was allowed to decompose in the presence of B_6H_{10} at room temperature, the data do not exclude the possibility that an intermediate generated from B_6H_{10} at higher temperatures reacts with B_8H_{12} to form this hydride.

In an attempt to determine the importance of the B_7 hydride intermediate in the formation of $B_{13}H_{19}$ and to establish a more systematic synthesis, the reaction scheme of eq 1 and 2 was devised. The thermally unstable $B_7H_{11}\cdot$

$$KB_7H_{12} + HCl(l) \xrightarrow{Me_2O} B_7H_{11}\cdot OMe_2 + H_2 \tag{1}$$

$$B_7H_{11}\cdot OMe_2 + BF_3 \xrightarrow{B_6H_{10}} BF_3\cdot OMe_2 + B_{13}H_{19} + H_2 \tag{2}$$

OMe_2 was obtained in essentially quantitative yield, but $B_{13}H_{19}$ could only be isolated in low yield from subsequent reaction with BF_3 and B_6H_{10}. The low yield suggests that most of the B_7H_{11} decomposes before it can be successfully trapped by the B_6H_{10}.

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Registry No. $B_{13}H_{19}$, 43093-20-5; B_6H_{10}, 23777-80-2; B_7H_{11}, 12430-08-9.

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Correspondence

Chemical Shifts of Carbon Atoms Bound to Transition Metals

AIC400985

Sir:

A large number of papers have recently appeared in which detailed rationalizations were supplied for the carbon-13 chemical shifts of carbon atoms bound to transition metals. We wish to point out that those rationalizations have been contradictory and misleading and also to suggest that in the coordination sphere of a transition metal simple explanations are unlikely to be valid.

Although traditional equations for calculation of carbon chemical shifts contain two terms, denoted "diamagnetic" and "paramagnetic"

$$\sigma = \sigma_d + \sigma_p \tag{1}$$

where σ_d reflects the screening due to electrons in the electronic ground state and σ_p screening due to the mixing of ground and excited states under the influence of the magnetic field, this is an artificial distinction which has meaning only in the context of the computational technique used.[1] In fact, as recently emphasized,[2] the relative magnitudes of the two terms depend upon the gauge chosen for the magnetic field vector potential A. Furthermore, calculations which do not involve gauge-invariant atomic orbitals (GIAO's) even produce values for the total screening constant, σ, which depend upon the choice of origin for the coordinate system.[3] (The use of GIAO's has lately begun to show excellent results for very simple molecules.[3-5])

So treatments of *total* screening constants in complex transition metal systems must be regarded with some suspicion and any which considers only that term traditionally called "paramagnetic" is almost certainly incomplete. The frequent assumption that variations in the "diamagnetic" term are negligible is doubtful. Flygare and Goodisman[6] have suggested a simple formula (later endorsed for homopolar molecules by Sadlej[7]) for estimating such effects, *i.e.*

$$\sigma_d = \sigma_d(\text{free atom}) + \frac{e^2}{3mc^2}\sum_\alpha \frac{Z_\alpha}{r_\alpha} \tag{2}$$

Application of a heuristically justified "local" version of this equation greatly improved the agreement between observed and calculated carbon-13 shifts in hydrocarbons.[8] A transition metal, particularly one of the third row, in light of this equation should produce enormous effects on the "diamagnetic" term of a directly bound carbon. For example, estimates of the second term in eq 2 of *ca.* 120, 190, and 340 ppm are appropriate to iron, ruthenium, and osmium, respectively. These will clearly vary between complexes. It is not surprising, then, that literature explanations of carbon-13 shifts in transition metal complexes on the basis of the "paramagnetic" term alone have frequently been contradictory.

An example of the difficulty in attributing principal causes

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to carbon shifts can be found in discussions of metal carbonyls. Various workers, most recently Bodner and Todd,[9] have proposed that the chemical shift of the carbonyl carbon atom is a linear measure of transition metal → carbonyl π back-donation. Available data[10,11] indicate that this linearity is only observed if the complexes are very closely related. Even $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ have chemical shifts of 212, 202, and 192 ppm, respectively. The suggestion[12] that the relationship applies to platinum carbonyl complex cations (where shifts of 19 ppm are observed with small changes (19 cm^{-1}) in ν_{CO}) is unlikely to be correct.

Another topic discussed from divergent viewpoints has been the shifts of π-bonded carbon atoms. One group[13] suggested that "nonbonded paramagnetic shielding effects" associated with partially filled metal d orbitals caused the upfield shift of π-bonded carbons upon coordination. The major evidence supporting this view was the observation of an approximately linear relationship between the shifts of π-bonded carbons and those of σ-bonded carbons in the same molecules. The proposal that slopes of $(R_{M-C_1}/R_{M-C_2})^3$ should be observed rested upon a misinterpretation of the theoretical work cited.[14,15] Finally the observation of only very small upfield shifts for olefins bound to d^{10} Ag(I)[16,17] is hardly a convincing argument for this shielding effect since ethylene bound to d^{10} Pt(0) in $PtL_2(C_2H_4)$ exhibits quite a marked upfield shift on complexation (+82.4 ppm),[18] as do olefins bound to Cu(I).[19]

Another group[18] suggested that the ^{13}C shifts in olefin complexes were due to changes in π-bond order resulting from metal–ligand π and π^* interactions: the metal only affects matters by altering the electron density in the various ligand molecular orbitals and hence the net bond orders within the original organic π system. If one quantifies this effect with the Pople "paramagnetic" term[20]

$$\sigma_p^{AA} = \frac{-e^2\hbar^2}{2m^2c^2(\Delta E)}\langle r^{-3}\rangle_{2p}\left(A_{AA} + \sum_{B\neq A} Q_{AB}\right) \qquad (3)$$

for any reasonable constant ΔE, the resulting simple calculations[21] show that such effects cannot by themselves account for the chemical shifts of carbon atoms π bonded to transition metals.

Two examples illustrate this clearly. First we consider π-cyclopentadienyl complexes. For any electron population reasonable in light of other physical measurements[22] and calculations,[23] shifts on complexation are calculated to be small (up to *ca.* 12 ppm for donation of 1.0 electron to the metal) and downfield of the resonance due to the free ligand. However, observed shifts for the complexed ligand vary over a considerable range, from 123.1 ppm for $C_5H_5TiCl_3$ to 63.9 ppm for $(C_5H_5)_2Os$.[24]

Second, the complexed π-allyl group also differs from its calculated pattern of behavior. Only the lowest two allyl ligand orbitals ($b_1(1)$ and a_2) interact significantly with palladium.[25] Thus, whereas the shift of the outer carbon atoms should vary markedly with the extent of delocalization of a_2, the nonbonding π orbital (an upfield shift of *ca.* 48 ppm/electron added), the central carbon atom shift is expected to vary little (less than 3 ppm) with such changes in both the bonding ($b_1(1)$) and nonbonding π orbitals; it should therefore be relatively independent of its environment. However, experimental results show that shifts of both types of atoms vary significantly from complex to complex,[24,26] even when only one metal is considered. More accurate molecular orbital calculations could be employed, but these would surely not affect the conclusion that the effects considered by this model are quantitatively unimportant. Any successful treatment of π-bonded carbon chemical shifts must take the effects of the transition metal more directly and completely into account.

It is noteworthy that two of the first workers[27] to measure ^{13}C chemical shifts in transition metal complexes concluded in 1965 that "No convincing explanation of these results within the framework of the current approximate shielding theory has been found." Such pessimism unfortunately is still warranted a decade later.

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Rhenium(I) Complexes of (*o*-Cyanophenyl)diphenylphosphine

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Sir:

Dinitriles and phosphinenitriles have recently been investigated as bidentate ligands potentially capable of coordinating through the nitrile group(s) π electrons. From spectroscopic and analytical data it has been proposed that (*o*-cyanophenyl)diphenylphosphine (L) forms dimeric π complexes with rhenium(I)[1] (**1**) and that both succinonitrile and L form monomeric π complexes with manganese(I)[1-3] (**2** and **3**). The ligand

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