Table I. Comparative ^{13}C and ^{19}F NMR Data for Fluoromethylidyne Clusters

compd	$\delta(^{13}C)$	$J(^{13}C,^{19}F)$,[a] Hz	$\delta(^{19}F)$	ref
$H_3Os_3(CO)_9(\mu_3\text{-}CF)$	212.5	371	−77.7	this work
$Co_3(CO)_9(\mu_3\text{-}CF)$	309	498	+44.5[b]	8, 9
$Fe_3(CO)_9(\mu_3\text{-}CF)_2$	365.8	452	+69.5	6

[a] These coupling constants can be assumed to have a negative sign, see ref 11. [b] The authors of ref 8 used a reversed sign convention. The positive sign is in accord with the current convention that shifts downfield are positive.

The formation of **2** from **1** and $AgBF_4$ presumably occurs by bromine abstraction to generate the cation $[H_3Os_3(CO)_9(\mu_3\text{-}C)]^+$. If the observed intermediate yellow color can be attributed to the cluster carbocation, it must have a significant lifetime. Fluorine abstraction from the tetrafluoroborate counterion apparently produces the fluoromethylidyne product, since, in the absence of excess BF_4^-, only a low yield of **2** is obtained. Attempts to observe this putative intermediate directly are underway.

The ^{13}C and ^{19}F NMR data collected for **2** are given in Table I together with the analogous data available for the compounds $Co_3(CO)_9(\mu_3\text{-}CF)$[8,9] and $Fe_3(CO)_9(\mu_3\text{-}CF)_2$.[6] The ^{19}F NMR signal for **2** occurs at −77.7 ppm, a much more shielded position than that observed for the fluorine nucleus in either of the other fluoromethylidyne compounds. This is likely due in part to a heavy-atom effect, since the series of compounds $[Co_2(CO)_6\{CpM(CO)_2\}(\mu_3\text{-}CF)]$ shows a sequential upfield shift as M = Cr (63.6 ppm) is replaced by Mo (38.4 ppm) and W (14.4 ppm).[5] This effect obviates useful comparison with the resonances of fluorine nuclei bound to nonmetallic units (e.g., FCH_2CH_3, −212 ppm; $FCMe_3$, −132 ppm, FCCH, −95 ppm).[10] The same effect apparently operates for ^{13}C NMR signals as well, since the fluoromethylidyne carbon in **2** resonates at significantly higher field than the corresponding carbons in either $Fe_3(CO)_9(\mu_3\text{-}CF)_2$ or $Co_3(CO)_9(\mu_3\text{-}CF)$ (vide infra). However, the carbon–fluorine coupling constant may be a better probe of the carbon environment, since it is significantly smaller in magnitude for **2** (371 Hz) than for either the tricobalt (498 Hz) or the triiron compound (452 Hz). Although coupling constants involving fluorine are not necessarily dominated by the Fermi-contact term,[11] the implication of a weaker C–F bond in **2** is consistent with our observation of ν(CF) at 1067 cm^{-1} compared with that reported for $Co_3(CO)_9(\mu_3\text{-}CF)$ at 1164 cm^{-1}.[4b]

Aime and co-workers have reported ^{13}C NMR chemical shift values for the substituted methylidyne carbon atoms in a series of compounds $Co_3(CO)_9(\mu_3\text{-}CX)$.[9] Combining our current ^{13}C NMR data for **2** with previous data obtained in our group (X = H, δ 119.2; X = Cl, δ 145.4; X = Br, δ 124.1; X = C_6H_5, δ 153.7) provides an analogous set of chemical shifts for the compounds $H_3Os_3(CO)_9(\mu_3\text{-}CX)$. As shown in Figure 1, there is a reasonably linear correlation between the two sets of data. Most interestingly, however, the chemical shift range of the methylidyne carbon atom for various substituents X covers 46 ppm in the tricobalt case, whereas it is twice as big, 93 ppm, for the triosmium analogues. Thus, the apical carbon center in the triosmium complexes is much more sensitive toward substituents with varying bonding properties.

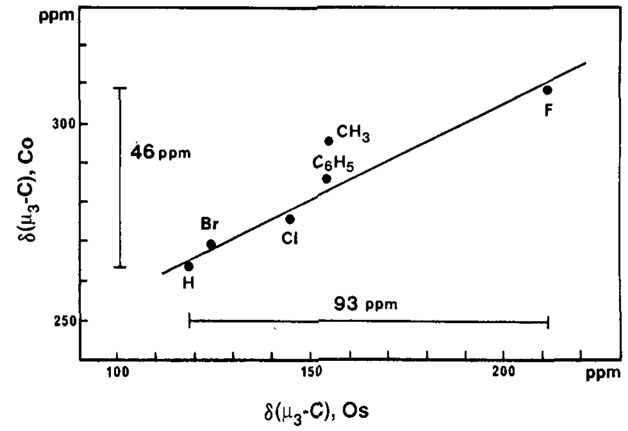

Figure 1. Comparison of the apical carbon ^{13}C NMR chemical shifts in $H_3Os_3(CO)_9(\mu_3\text{-}CX)$ and $Co_3(CO)_9(\mu_3\text{-}CX)$ (X = H, Cl, Br, C_6H_5, CH_3, F). The chemical shift for $H_3Os_3(CO)_9(\mu_3\text{-}CCH_3)$ (154.7) was reported in ref 13.

An explanation for this observation is suggested by work comparing $Co_3(CO)_9(\mu_3\text{-}CX)$ and $H_3Ru_3(CO)_9(\mu_3\text{-}CX)$ clusters in terms of photoelectron spectroscopy and MO calculations.[12] The apical carbon bonding in the tricobalt clusters is more delocalized, with extensive mixing of Co–Co and Co–C interactions, whereas the bridging hydrogens in the triruthenium clusters disrupt the metal–metal bonding and leave the Ru–C interactions more distinct. Extending these results to the congeneric triosmium complexes indicates that the methylidyne carbon in $H_3Os_3(CO)_9(\mu_3\text{-}CX)$ clusters will be more isolated electronically than that in $Co_3(CO)_9(\mu_3\text{-}CX)$ clusters and therefore less able to delocalize the electronic effects of changing the substituents. This variability in response complicates the issue of identifying characteristic chemical shifts for specific ligands in clusters for comparison with chemisorbed surface species.[13]

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Signs of Interphosphorus Nuclear Spin Coupling Constants in Octahedral Transition-Metal Complexes Containing Chelated Phosphine Ligands

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In a recent comment by Baker and Field[1] on internuclear spin–spin coupling in formally octahedral transition-metal phosphine complexes, it was claimed that the sign of ^2J(PMP) for pairs of cis-related phosphorus atoms is generally negative and that this could be used as a basis for spectral assignments. We wish to point out that our own published and unpublished results[2–6] demonstrate that this is not the case, particularly when chelating ligands are involved, as they are in the examples cited by Baker and Field.[1]

It was proposed a decade ago by Grim et al.[7] that the couplings formally described as ^2J(PMP) in cis diphosphine chelate com-

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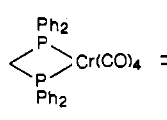
plexes are in fact the algebraic sums of "through-the-metal" and "backbone" contributions, which may be of opposite sign. This additive approach to coupling in ring compounds has subsequently been applied to other types of compounds, for example cyclic stanna-[8] and platinaalkanes.[9] In transition-metal phosphine complexes, recent work using multiple-resonance techniques[2] has shown that the through-the-metal contribution is negative in carbonyl compounds of chromium(0), molybdenum(0), and tungsten(0) and that the backbone contribution can be of either sign depending on the length of the backbone and the type and hybridization of the atoms in it. This leads to dramatic variations in the magnitudes *and the signs* of $^2J(\mathrm{PMP})_{\mathrm{cis}}$ in such complexes. As examples we cite values of −13.0, +47.0, 0 ±0.5, and +21 Hz in **1**, **2**, and **3**,[2] and in **4**,[6] respectively. More strikingly, in **5** the three values of $^2J(\mathrm{PMP})_{\mathrm{cis}}$ are −18.3, +17.6, and −17.2 Hz for P_AP_B, P_AP_C, and P_BP_C, respectively.[3] Similarly, in **6** they are +25 and +87 Hz for P_AP_B and P_CP_D, respectively, whereas the couplings for P_AP_C, P_BP_C, and P_BP_D, which do not have backbone contributions, are −20, −19, and −20 Hz, respectively, the trans coupling for P_AP_D being +87 Hz.[4]



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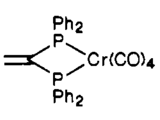

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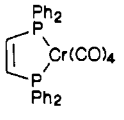

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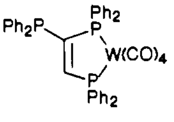

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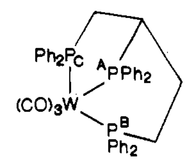

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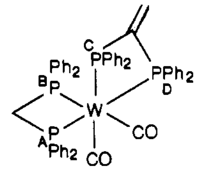

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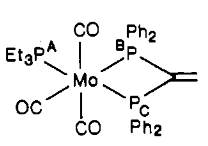

7

Although much of this variation is due to changes in the ligand backbone, there is also a dependence on the characteristics of the metal center, and work on carbonyl complexes of the tridentate ligand $(\mathrm{Ph_2P})_2\mathrm{CHCH_2PPh_2}$ has confirmed values of ca. −41, −30, and −22 Hz for the through-the-metal contributions for chromium(0), molybdenum(0), and tungsten(0), respectively.[5] For square-planar palladium(II) and platinum(II) the corresponding figures are ca. −15 and −32 Hz.[6] These ranges are large enough to suggest that when certain substituents are present or when other factors such as bond-angle constraints are operative, through-the-metal contributions might well in some cases become positive. An additional important consequence is that large backbone contributions can lead to an inversion of the general rule[10,11] that states that trans $^2J(\mathrm{PMP})$ couplings are larger than their cis counterparts. For example, in **7** the cis coupling for P_BP_C is +79 Hz, whereas the trans one for P_AP_C is smaller at +69 Hz, the coupling for the nonchelated P_AP_B pair being "normal" at −24 Hz.[4]

It is thus clear that while the signs given for the geminal interphosphorus couplings in the particular ruthenium complexes cited by Baker and Field[1] are correct, it is not generally true to claim that they will always or even normally be negative in all transition-metal complexes, and it is essential to undertake appropriate experimental sign determinations. In this context it should be noted that while spectral analysis can often give the relative signs of certain coupling constants or combinations of them, it cannot always lead to a complete set. However, selective multiple-resonance[2,5,6] or two-dimensional[4] experiments will usually provide an unambiguous solution.

Acknowledgment. We thank the SERC for support.

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Preparation and Crystal Structure of a New Type of Triply Bridged Pyrazabole[1]

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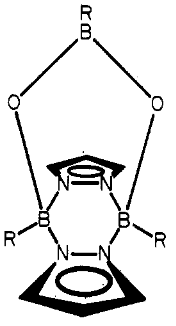
The reaction of *B*-triorganylboroxins, $(-\mathrm{BRO}-)_3$, with pyrazole, Hpz, has recently been found to yield a novel type of pyrazabole in which the two boron atoms of a pyrazabole skeleton, $\mathrm{B}(\mu\text{-pz})_2\mathrm{B}$, are linked by a third bridging unit, i.e., O–BR–O, as shown in **1**.[2] Subsequently, such species have been observed as products in various other reactions, suggesting that the framework of **1** is chemically quite stable. Since part of the original boroxin framework is preserved in **1**, it was assumed that other boron heterocycles should react with pyrazole in analogous fashion. However, the reaction of borazines, $(-\mathrm{BRNR'}-)_3$, with pyrazole unexpectedly led to (μ-amido)(μ-pyrazolato)diboron species, **2**, which are relatives of the pyrazaboles but do not feature the $\mathrm{B_2N_4}$ skeleton of a pyrazabole.[3] In the search for true analogues of **1**, i.e., triply bridged pyrazaboles but with a unit other than O–BR–O as the third bridge between the two pyrazabole boron atoms, the reaction of a 1,2,4,3,5-dithiaazadiborolidine with pyrazole has been studied.



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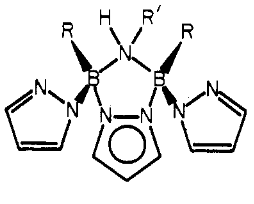

2

Experimental Section

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Melting points (uncorrected) were determined on a Mel-Temp block.

NMR spectra were recorded on solutions in $\mathrm{CDCl_3}$ on a Varian XL-200 instrument. Chemical shift data are given in ppm with positive values indicating downfield shift from the reference (internal $\mathrm{Me_4Si}$ for ^{1}H NMR, external $\mathrm{Et_2O{\cdot}BF_3}$ for ^{11}B NMR); s = singlet, d = doublet,

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