on the arylcarbenium ions, $ArCH_2^+$.[8]

It is evident from Table I and consideration of the ion structures that the largest isotope shifts are observed at positions to which substantial charge is delocalized. Isotope shifts for **1**–**3** are plotted vs. q_π in Figure 1. A very good correlation is obtained ($\Delta\delta_c = 1.052q_\pi - 0.002$; correlation coeff = 0.976) including even the ortho- and peri-type positions. It is interesting to note that an upfield shift is observed at C-4a in **2** where a negative charge is predicted. The simple correlation of ^{13}C chemical shifts vs. charge for the same set of carbons is considerably worse: $\delta_c = 118.1q_\pi + 129.0$; correlation coeff = 0.888. The δ_c vs. charge correlation is poor primarily because of the substantial upfield shifts displayed by the ortho- and peri-type carbons due to the steric proximity of the methyl groups.[8]

The quality of the correlation in Figure 1 for hydrocarbon arylcarbenium ions is sufficiently good to view the isotope shift as a probe of charge distribution in such systems and to suggest that perturbation of hyperconjugation is the principal source of the long-range isotope shifts. However, the results for ion **4** indicate an intriguing nonequivalence of shifts for the ortho carbons. The ortho positions in **4** differ by 0.081 ppm,[9] with $\Delta\delta_c$ of 0.11 ppm for one position and 0.03 ppm for the other. If the isotope shifts were purely hyperconjugative in origin, transmitted through the π-system by a simple reduction in electron supply to the carbenium center, the ortho isotope shifts would be identical, and exactly half the magnitude of the shifts for **1**. Instead, one ortho carbon resonance in **4** is more deshielded and the other is less deshielded than by the expected 0.085 ppm.

The chemical shift nonequivalence in **4** raises the possibility of a *through-space* isotopic perturbation of resonance,[10] which shifts charge from one ortho position to the other. We make a tentative assignment of the more deshielded ortho carbon as being syn to the deuterated methyl,[11] on the presumption that deuteration diminishes through-space orbital interactions, similar to hyperconjugation, that have been postulated to account for part of the shielding by syn methyl groups.[12] In resonance terms, canonical form **4a** is suggested to contribute more than **4b**. The alternative origin for the effects in **4** of a stereochemically dependent effect operating through σ bonds seems less likely, because isotope shifts through more than three bonds are usually very small. Similarly, an isotope shift arising from perturbation of a steric interaction with the ortho C–H bond seems unlikely because no such isotope shift was found in even more crowded saturated systems.[13] In neutral systems related to **1** and **4**, we find no detectable (<0.008 ppm) isotope shift at ortho carbons in 2-chloro-2-phenylpropane-*1,1,1,3,3,3*-d_6 and small $\Delta\delta_c$ of 0.025 and 0.010 ppm at ortho and para carbons, respectively, in 2-phenylpropene-*1,1,3,3,3*-d_5. It is clear that further experimental and theoretical study will be required to establish the precise origin of the unusual ortho effects in **4**.[14]

An additional indication of a through-space effect may be the isotope shift for the peri carbon, C-8, in the 1-naphthyl system, **2**. The data point for this position deviates most from the correlation line in Figure 1, and the deviation is in the direction of a larger downfield shift than predicted. A small downfield isotope shift of apparent through-space origin has also been reported in deuterated methylcyclophanes.[5]

In conclusion, long-range shifts induced by isotopic perturbation of hyperconjugation can serve as a probe of π charge distribution. However, such shifts must be significantly larger than those produced by through-bond or other effects.[3,7,15] Effects through three bonds are well-known,[3,13] and in the cations described here, positions near the site of substitution may experience isotope shifts that are not due to a simple perturbation of electron supply to the π-system. Thus, the NMR isotope shifts may reliably reflect charge effects only at sterically remote positions.

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Registry No. 1, 75296-07-0; **2**, 86688-67-7; **3**, 86688-68-8; **4**, 86688-69-9.

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[9] The peak separation was obtained from an independent measurement with only the labeled ion present.

[10] The concept of isotopic perturbation of resonance was introduced by: Saunders, M.; Kates, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 8071–8072.

[11] This assignment is supported by our unpublished observations of isotope shifts at C-3 in (2-thienyl)methylcarbenium ion, for which *E* and *Z* isomers are known: Forsyth, D. A.; Olah, G. A. *J. Am. Chem. Soc.* **1979**, *101*, 5309–5316.

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Metallacumulenes: A Diruthenium Vinylidene–Alkylidene Complex from the Apparent Dimerization of $[Ru(C{=}C{=}CMe_2)(PPh_3)_2(Cp)][PF_6]$

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Only recently have reliable methods for the preparation of metal allenylidene complexes ($M{=}C{=}C{=}CR_2$) been developed,[1] and their chemistry remains largely unexplored.[1b,e] We previously reported that diphenylallenylidene complex Ia resulted from reaction 1.[1a] This reaction takes a different course when 2-methyl-3-butyn-2-ol is the substrate.

$$[RuClL_2(Cp)] + HC{\equiv}CC(OH)R_2 + NH_4PF_6 \rightarrow [Ru(C{=}C{=}CR_2)L_2(Cp)][PF_6] \quad (1)$$

Ia, L = PMe$_3$; R = Ph
Ib, L = PPh$_3$; R = Me

A mixture of 1.0 g (1.4 mmol) of $[RuCl(PPh_3)_2(Cp)]$, 0.67 g (4.1 mmol) of NH_4PF_6, and 0.35 mL (5.2 mmol) of $HC{\equiv}CC(OH)Me_2$ in dry methanol (50 mL) was stirred for 21 h at room temperature, during which time the color changed from orange to deep purple. The volatile components were removed in vacuo, and the residue was recrystallized from dichloromethane/ethyl ether to give 1.2 g (97%) of a microcrystalline, red-purple solid (II).[2] Slow recrystallization from dichloromethane/ethyl ether produced crystals suitable for X-ray diffraction. Crystal structure analysis[4] revealed that product II is a *dimer* of the expected

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[2] ^1H NMR (90 MHz, $(CD_3)_2CO$ δ 7.7–7.0 (ca. 61 H, m, aromatic and vinyl), 6.24 (1 H, s, C=CH), 5.63 (5 H, s, Cp), 5.07 (5 H, s, Cp′), 3.67 (2 H, s, CH_2), 1.50 (2 H, s, CH_2'); IR (mull) 1565 (m, C=C)[3], 835 (vs, $[PF_6]^-$) cm^{-1}. Anal. ($C_{92}H_{82}F_{12}P_6Ru_2$) C, H, P.

[3] (a) Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7763–7765. (b) Bruce, M. I.; Wallis, R. C. *Aust. J. Chem.* **1979**, *32*, 1471. (c) Berke, H. *Z. Naturforsch., B* **1980**, *35B*, 86–90. (d) Berke, H.; Huttner, G.; von Seyerl, J. *J. Organomet. Chem.* **1981**, *218*, 193–200.

[4] Crystal data for compound II: space group $P\bar{1}$, $a = 13.172$ (4) Å, $b = 15.344$ (3) Å, $c = 22.026$ (5) Å, $\alpha = 71.68$ (3)°, $\beta = 75.72$ (3)°, $\gamma = 85.93$ (2)°, $V = 4095.41$ Å^3, $Z = 2$, $\rho_{calcd} = 1.463$ g·cm^{-3}, $\mu = 5.86$ cm^{-1}. The structure was solved using MULTAN 77 to locate the two ruthenium atoms and two of the phosphorus atoms by direct methods, and the remaining atoms were found from subsequent difference Fourier maps. The 72 carbon atoms belonging to the 12 phenyl rings were treated as rigid groups. Hydrogen atoms were placed in idealized positions and were not refined. All other atoms were refined using anisotropic thermal parameters. Refinement by full-matrix least-squares procedures led to $R = 7.9\%$, $R_w = 9.6\%$ using 5203 reflections with $F^2 \geq 3\sigma(F^2)$.

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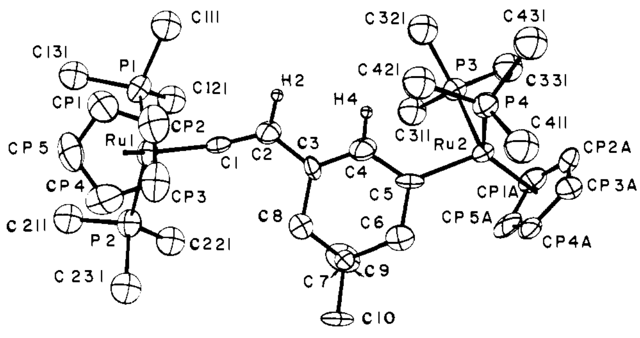


Figure 1. Perspective ORTEP diagram of the central portion of the dication of $[Ru_2(\mu\text{-}C_{10}H_{12})(PPh_3)_4(Cp)_2][PF_6]_2$ (II) showing 50% probability ellipsoids. Only one atom of each of the 12 phenyl rings is illustrated. The hydrogen atoms are placed in calculated positions and are arbitrarily scaled.

Table I. Selected Bond Distances and Angles with Errors for $[Ru_2(\mu\text{-}C_{10}H_{12})(PPh_3)_4(Cp)_2][PF_6]_2$

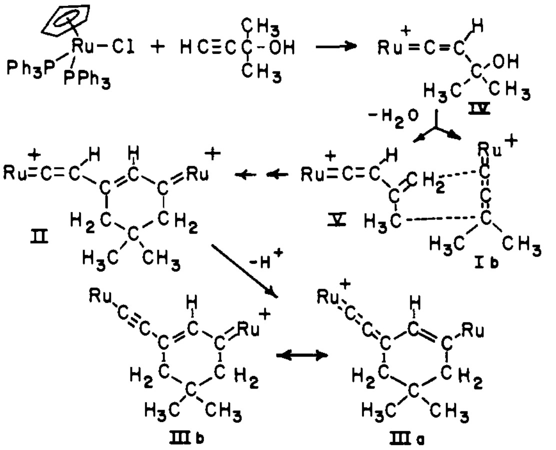
bond	distance, Å	atoms	angle, deg
Ru1-C1	1.83 (2)	Ru1-C1-C2	166 (1)
Ru1-P1	2.368 (5)	C1-C2-C3	127 (2)
Ru1-P2	2.381 (5)	C2-C3-C4	120 (1)
Ru1-CPO[a]	1.93 (3)	C2-C3-C8	118 (1)
Ru2-C5	2.30 (2)	C4-C3-C8	122 (1)
Ru2-P3	2.347 (5)	C3-C4-C5	125 (1)
Ru2-P4	2.354 (5)	Ru2-C5-C4	124 (1)
Ru2-CPOA[a]	1.92 (1)	Ru2-C5-C6	123 (1)
C1-C2	1.29 (2)	C4-C5-C6	112 (1)
C2-C3	1.45 (2)	C5-C6-C7	118 (1)
C3-C4	1.37 (2)	C6-C7-C8	107 (1)
C4-C5	1.46 (2)	C7-C8-C3	114 (1)
C5-C6	1.49 (2)		
C6-C7	1.57 (2)		
C7-C8	1.50 (2)		
C7-C9	1.52 (2)		
C7-C10	1.56 (2)		
C8-C3	1.51 (2)		

[a] CPO and CPOA are the centroids of the cyclopentadienyl rings CP1-CP5 and CP1A-CP5A, respectively.

dimethylallenylidene complex Ib. The central portion of the dication is illustrated in Figure 1. Two typical $[Ru(PPh_3)_2(Cp)]$ moieties[5] are bonded to a bridging $C_{10}H_{12}$ ligand, which can be viewed as resulting from formation of two carbon–carbon bonds (C4–C5 and C8–C7) between two $C{=}C{=}CMe_2$ ligands, with concomitant proton shifts. The Ru1–C1–C2–C3 group comprises a vinylidene linkage, as suggested by a short Ru1–C1 bond and a nearly linear bond angle at C1 (see Table I). The second ruthenium atom is bonded to the cyclohexene ring by an alkylidene (carbene) bond between Ru2 and C5. The atoms C1, C2, C3, C4, C5, and Ru2 are nearly coplanar (maximum deviation is 0.05 Å for C4), suggesting conjugation along this chain. There is a dihedral angle of 86.8° between the planes Ru1–C1–CP0 (CP0 is the centroid of the ring CP1–CP5) and C1–C2–C3. The planes Ru2–C5–CP0A (CP0A is the centroid of the ring CP1A–CP5A) and C4–C5–C6 form a dihedral angle of 18.4°, with the vinylic carbon C4 oriented "trans" to the cyclopentadienyl ring. These values are roughly consistent with Hoffmann's predictions of 90° and 0° for $[Fe(CO)_2(Cp)]$ model compounds.[6] In addition to the dication, the unit cell of the crystal includes two slightly disordered $[PF_6]^-$ ions and a water molecule.[7]

The dication II dissolves in dry, polar organic solvents to give deep, red-purple solutions ($\lambda_{max} = 498$ nm, $\epsilon = 1.2 \times 10^4$) that are stable to dry air for days. Solutions of II become deep blue-violet ($\lambda_{max} = 575$ nm, $\epsilon = 1.9 \times 10^4$) upon extended exposure to atmospheric moisture or addition of triethylamine. The resulting blue-violet product (III) is best isolated by chromatography on alumina. Spectroscopic evidence[8] suggests that the vinylidene β-proton is removed from II to give $[Ru_2(\mu\text{-}C_{10}H_{11})(PPh_3)_4(Cp)_2][PF_6]$ (III), which can be regarded as the resonance hybrid of an allenylidene–vinyl complex (IIIa in Scheme I) and an alkynyl–alkylidene complex (IIIb). Addition of a strong acid (e.g., trifluoroacetic) to III regenerates II; this reversible reaction can be monitored by visible or NMR spectroscopy.

Scheme I. Pathway for the Formation and Deprotonation of $[Ru_2(\mu\text{-}C_{10}H_{12})(PPh_3)_4(Cp)_2][PF_6]_2$ (II)



Remarkable regioselectivity is demonstrated in the formation of the two new carbon–carbon bonds. Scheme I outlines a possible pathway leading to II. The alkynol most probably reacts with the ruthenium chloride (dissociated in methanol[9]) to give an intermediate hydroxyvinylidene complex IV, which spontaneously dehydrates to a dimethylallenylidene cation (Ib), an isopropenylvinylidene cation (V), or both. Bond formation between the two δ-carbons of V (which should be nucleophilic, at least upon deprotonation[10]), and the α- and γ-cations of Ib (which should be electrophilic[1b,11]) probably occurs in a stepwise manner. The several requisite proton shifts should be facile in the reaction medium. No precedent for a dimerization of this type has been found in either heterocumulene[12] or vinyl cation chemistry.[13] Reactions that model certain possible bond-forming steps are now under investigation.

Acknowledgment. We thank the Research Corporation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and Occidental Research Corporation for financial assistance, Engelhard Industries and Johnson Matthey, Inc., for loans of $RuCl_3$, Dow Chemical for a generous

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(7) A residual electron density peak, not within bonding distance of any other atom, was refined as an oxygen atom (O1). It is presumably part of a water molecule although no associated protons were located.

(8) ^1H NMR (90 MHz, $(CD_3)_2CO$) δ 7.5–7.0 (m, ca. 61 H, aromatics and vinyl), 4.75 (s, 5 H, Cp), 4.50 (s, 5 H, Cp′), 3.40 (s, 2 H, CH_2), 1.33 (s, 2 H, CH_2'), 0.80 (s, 6 H, CH_3); IR (mull) 1970 (m, $C{=}C{=}C$), 835 (s, $[PF_6]^-$) cm^{-1}. Anal. ($C_{92}H_{81}F_6P_5Ru_2$) C, H, P.

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(12) (a) A different type of dimerization occurs upon attempting to prepare $[Cr(C{=}C{=}CMe_3)(CO)_5]$ from $[Cr(CO)_6]$ and $Li_2[C{\equiv}CCMe_2O]$.[1c] (b) Protonation of $[Fe(C{\equiv}CPh)(CO)_2(Cp)]$ or deprotonation of $[Fe(C{=}CH_2)(CO)(PR_3)(Cp)]^+$ both lead to cationic diiron cyclobutenylidene complexes *via* a related cyclization. Davison, A.; Solar, J. P. *J. Organomet. Chem.* **1978**, *155*, C8. Kolobova, N. Y.; Skripkin, V. V.; Aleksandrov, G. G.; Struchkov, Yu. T. *Ibid.* **1979**, *169*, 293 and ref 11e. (c) Ulrich, H. "Cycloaddition Reactions of Heterocumulenes"; Academic Press: New York, **1967**.

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gift of Q1 catalyst, and Martin Stiles for helpful discussions.

Supplementary Material Available: Listings of positional and thermal atomic parameters for nongroup atoms (Table II), group atoms (Table III), and hydrogen atoms (Table IV) and experimental and calculated structure factors (Table V) (39 pages). Ordering information is given on any current masthead page.

Insertion of Boron into an Osmium–Carbonyl Bond. Preparation and Structure of the Carbonyl Borylidyne $(\mu\text{-H})_3(\mathrm{CO})_9\mathrm{Os}_3\mathrm{BCO}$

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From the hydroboration of the unsaturated cluster $(\mu\text{-H})_2\mathrm{Os}_3(\mathrm{CO})_{10}$, the first example of a carbonyl borylidyne transition-metal cluster $(\mu\text{-H})_3(\mathrm{CO})_9\mathrm{Os}_3\mathrm{BCO}$ (I) has been prepared through the insertion of boron into a metal–carbonyl bond. Compound I is an analogue of the known carbonyl methylidyne complexes $(\mu\text{-H})_2(\mathrm{CO})_9\mathrm{Os}_3\mathrm{CCO}$, $(\mu\text{-H})_3(\mathrm{CO})_9\mathrm{Os}_3\mathrm{CCO}^+$, and $(\mathrm{CO})_9\mathrm{Co}_3\mathrm{CCO}^+$.[1-3] The arrangement of non-hydrogen atoms in the molecular structure of $(\mu\text{-H})_3(\mathrm{CO})_9\mathrm{Os}_3\mathrm{BCO}$ (Figure 1) is like that of $(\mu\text{-H})_2(\mathrm{CO})_9\mathrm{Os}_3\mathrm{CCO}$.[1]

Compound I was prepared according to reaction 1. No apparent reaction occurred unless both $\mathrm{BH}_3\mathrm{NEt}_3$ and $\mathrm{B}_2\mathrm{H}_6$ were present. Scheme I accounts for this requirement. In this scheme an initial adduct, **1**, of $\mathrm{BH}_3\mathrm{NEt}_3$ to $(\mu\text{-H})_2\mathrm{Os}_3(\mathrm{CO})_{10}$ is believed to occur through the formation of a B–H–Os bond. Abstraction of NEt_3 by the free $\mathrm{B}_2\mathrm{H}_6$ in the system would allow formation of the metalloboranes **2a** and **2b** followed by an irreversible step involving insertion of boron into an osmium–carbonyl bond of the $\mathrm{Os(CO)}_4$ unit with concomitant reductive elimination of H_2. The proposed intermediate **2b** is similar in structure to that assigned to its analogue $\mathrm{Os}_3(\mathrm{CO})_{10}\mathrm{CH}_4$.[4,5]

$$(\mu\text{-H})_2\mathrm{Os}_3(\mathrm{CO})_{10} + {}^1\!/_2\mathrm{B}_2\mathrm{H}_6 \xrightarrow[\mathrm{CH_2Cl_2}]{\mathrm{BH_3NEt_3}} (\mu\text{-H})_3(\mathrm{CO})_9\mathrm{Os}_3\mathrm{BCO} + \mathrm{H}_2 \quad (1)$$

According to Scheme I, $\mathrm{BH}_3\mathrm{NEt}_3$ is regenerated as reaction 1 proceeds to completion. To test this point, reaction 1 was followed by ^{1}H NMR spectroscopy. No apparent diminution in $\mathrm{BH}_3\mathrm{NEt}_3$ concentration was observed even as the reaction approached completion.

In a typical synthesis, I was prepared from a mixture of $(\mu\text{-H})_2\mathrm{Os}_3(\mathrm{CO})_{10}$ (0.164 mmol), $\mathrm{B}_2\mathrm{H}_6$ (0.082 mmol), and $\mathrm{BH}_3\mathrm{NEt}_3$ (0.164 mmol) in 12 mL of $\mathrm{CH}_2\mathrm{Cl}_2$, stirred for 3 days at room temperature. It was obtained in 85% yield (0.139 mmol) as a bright yellow solid [Infrared in cyclohexane (ν_{CO}): 2120 w, 2094 s, 2040 s, 2015 m, 1969 w(br) cm^{-1}] and H_2 was produced in 91% yield (0.149 mmol). It was also obtained when THF replaced NEt_3. However when excess THF was used, another cluster system formed, $[(\mu\text{-H})_3\mathrm{Os}_3(\mathrm{CO})_9]_3(\mathrm{B}_3\mathrm{O}_3)$.[6]

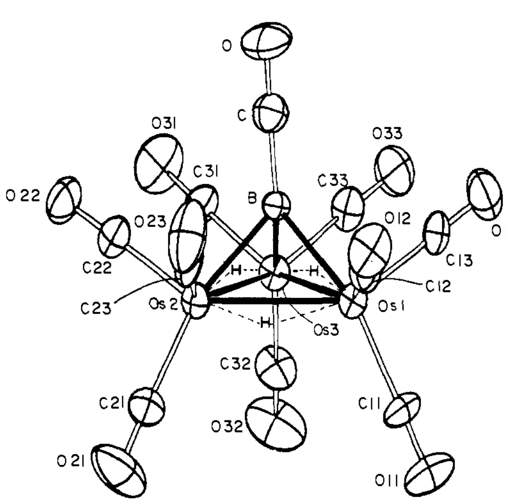
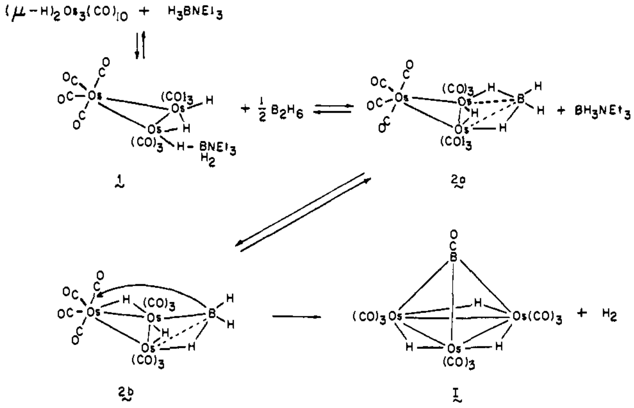


Figure 1. Molecular structure of $(\mu\text{-H})_3(\mathrm{CO})_9\mathrm{Os}_3\mathrm{BCO}$.

Scheme I



The ^{13}C NMR spectrum of $(\mu\text{-H})_3(\mathrm{CO})_9\mathrm{Os}_3\mathrm{BCO}$ is consistent with its molecular structure (Figure 1) in that three different types of carbon are present in the ratio of about 1:3:6. Three hydrogens in this compound are revealed by the ^{11}B NMR spectrum[8], which is a quartet (1:3:3:1), and the ^{1}H NMR signal has a chemical shift consistent with the presence of Os–H–Os bridges.[9]

Compound I is stable in air. It sublimes in vacuum (60 °C). There is no apparent ^{13}CO–^{12}CO exchange between ^{13}CO (1 atm) over a solution of $(\mu\text{-H})_3(\mathrm{CO})_9\mathrm{Os}_3\mathrm{BCO}$ in $\mathrm{CH}_2\mathrm{Cl}_2$ (2 days, 25 °C). However, CO is quantitatively displaced from boron by 1 equiv of $\mathrm{P(CH_3)_3}$ in $\mathrm{CH}_2\mathrm{Cl}_2$ (1 day, 25 °C) to form $(\mu\text{-H})_3(\mathrm{CO})_9\mathrm{Os}_3\mathrm{BP(CH_3)_3}$ (**II**) (reaction 2). The ^{11}B NMR spectrum,[10]

$$(\mu\text{-H})_3(\mathrm{CO})_9\mathrm{Os}_3\mathrm{BCO} + \mathrm{P(CH_3)_3} \rightarrow (\mu\text{-H})_3(\mathrm{CO})_9\mathrm{Os}_3\mathrm{BP(CH_3)_3} + \mathrm{CO} \quad (2)$$

a doublet, and the ^{31}P NMR spectrum,[11] a quartet (1:1:1:1), indicate that the $\mathrm{P(CH_3)_3}$ group is bound to boron.

The molecular structure of $(\mu\text{-H})_3(\mathrm{CO})_9\mathrm{Os}_3\mathrm{BCO}$[12] has approximate C_{3v} symmetry (Figure 1). Although the three hydrogens

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(7) ^{13}C NMR spectrum ($\mathrm{CH}_2\mathrm{Cl}_2$, 50% ^{13}CO enriched, 25 °C) δ 193.3 (1, CO, quartet 1:1:1:1), $J_{\mathrm{B-C}} = 88$ Hz), 171.5 (3, CO, s), 168.2 (6, CO, d, $J_{\mathrm{C-H}} = 8.5$ Hz), 0.00 ($\mathrm{Me_4Si}$).

(8) ^{11}B NMR spectrum ($\mathrm{CD}_2\mathrm{Cl}_2$, 25 °C) δ 19.4 [quartet (1:3:3:1), $J_{\mathrm{B-H}} = 3$ Hz] 0.00 ($\mathrm{BF_3OEt_2}$).

(9) ^{1}H NMR spectrum ($\mathrm{CD}_2\mathrm{Cl}_2$, 25 °C) τ 29.8, 10.00 ($\mathrm{Me_4Si}$).

(10) ^{11}B NMR spectrum (CDCl_3, 25 °C) δ 60.9 (d, $J_{\mathrm{B-P}} = 118$ Hz).

(11) ^{31}P NMR spectrum ($\mathrm{CH}_2\mathrm{Cl}_2$, 25 °C) δ 16.3 [quartet (1:1:1:1), $J_{\mathrm{BP}} = 118$] 0.00 ($\mathrm{H_3PO_4}$).

(12) Crystal data for $(\mu\text{-H})_3(\mathrm{CO})_9\mathrm{OsBCO}$: Space group $P\bar{1}$, $a = 9.203$ (2) Å, $b = 12.608$ (2) Å, $c = 8.188$ (2) Å, $\alpha = 80.93$ (2)°, $\beta = 111.43$ (2)°, $\gamma = 87.73$ (2)°, $V = 833.2$ (6) Å^3, ρ(calcd) = 3.44 g cm^{-3} for M$_r$ 864.41, $Z = 2$. Diffraction data were collected with an Enraf-Nonius CAD4 diffractometer. Crystallographic computations were carried out on a PDP 11/44 computer using the SDP (structure determination package). The structure was solved by interpreting the Patterson map, difference Fourier syntheses, and full-matrix least-squares refinement. $R_F = 0.077$ and $R_{WF} = 0.095$ for 4083 reflections [$I > 3.0\sigma(\mathrm{I})$] of 5366 reflections collected in the range of $4° \leq 2\theta \leq 60°$ (Mo Kα radiation).

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