the product. In the second mechanism, the metallaoxanorbornadiene results from direct attack of the β-ester carbonyl oxygen atom on the cobalt atom of the initial metallacyclopentene (Scheme II). Cobaltaoxanorbornadienes must be considered as intermediates in the reactions of cobaltacyclopentenes if the second mechanism is correct and the rate of this reaction is sufficiently fast. The mechanism of the reaction of 2 with ligands to reform 1 must be the microscopic reverse of the formation of 2. Study of the reactions of 2 will provide considerable information about the mechanism of cobaltacyclopentene reactions and may permit the determination of several fundamental rate constants for the system. Furthermore, such reactions provide a means of preparing cobaltacyclopentene complexes substituted with potentially reactive ligands that are inaccessible from 1. Investigations of the reactions of these complexes will afford a test of whether prior coordination of a ligand is necessary for reaction with cobaltacyclopentenes. Several of these points are currently being investigated in our laboratories.

Nucleophilic Additions to Carbonyl Ligands on Tetracobalt Clusters. Formation of Polynuclear Formyl and Carbene Complexes

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The tetracobalt cluster $Co_4(CO)_{10}(\mu_4\text{-PPh})_2$ (I) undergoes facile reductive decarbonylation to afford the bridged hydride $Co_4(CO)_9(PPh)_2(\mu\text{-H})^-$ in quantitative yields upon the treatment with various types of borohydrides at 25 °C. However, when the reductions are carried out at −78 °C, a transient intermediate can be detected and its structure shown to be the corresponding formyl derivative $Co_4(CO)_9(PPh)_2CHO^-$ (III) from its IR spectrum and ^1H and ^{13}C NMR spectra. The formation of the formyl intermediate III is confirmed by deuterium-labeling studies, and its spontaneous decarbonylation to the μ-hydride is described. Nucleophilic addition to a CO ligand as a route to the formyl intermediate is demonstrated by the generation of the corresponding acyl analogues in excellent yields following the treatment of I with methyl- and n-butyllithium. The formyl and acetyl tetracobalt clusters are efficiently trapped by O-alkylation with methyl triflate to afford the carbene derivatives $Co_4(CO)_9(PPh)_2[\mu\text{-C(OMe)H}]$ and $Co_4(CO)_9(PPh)_2[\mu\text{-C(OMe)Me}]$, respectively. Nucleophilic addition to I followed by alkylation to afford these tetracobalt carbene derivatives is thus analogous to the behavior of the triosmium cluster $Os_3(CO)_{12}$ recently reported by Kaesz and co-workers. The acid-catalyzed 1,2-elimination of methanol from the carbene cluster $Co_4(CO)_9(PPh)_2[\mu\text{-C(OMe)Me}]$ yields the vinylidene cluster $Co_4(CO)_9(PPh)_2(\mu\text{-C=CH}_2)$, which is also produced in high yields when the acetyl cluster is treated with trifluoroacetic anhydride. The molecular structures of $Co_4(CO)_9(PPh)_2[\mu\text{-C(OMe)Me}]$ and the vinylidene derivative are established by X-ray crystallography. $Co_4(CO)_9(PPh)_2[\mu\text{-C(OMe)Me}]$ crystallizes in the monoclinic space group $P2_1/c$ with $a = 16.465$ (2) Å, $b = 23.987$ (3) Å, $c = 15.775$ (2) Å, $\beta = 112.61$ (1)°, $V = 5752$ Å^3, and $Z = 8$. $Co_4(CO)_9(PPh)_2(\mu\text{-C=CH}_2)$ crystallizes in the monoclinic space group $P2_1/n$ with $a = 9.954$ (1) Å, $b = 12.865$ (3) Å, $c = 10.270$ (1) Å, $\beta = 98.88$ (1)°, $V = 1299$ Å^3, and $Z = 2$. Reactivity studies of the formyl and the various carbene ligands bound to the tetracobalt cluster are described.

Introduction

Polynuclear clusters with contiguous metal centers that can promote the multisite activation of substrates may be suitable models for carbon monoxide reduction.[1,2] The synthesis and reactivity of polynuclear metal clusters that contain formyl, alkyl, hydrido, and alkylidene ligands continue to attract interest as reactive intermediates.[3,4]

Among such polynuclear clusters, we have focused our attention on the bicapped tetracarbonyl carbonyl I since

I
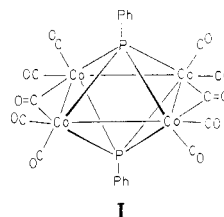
(1) (a) Muetterties, E. L.; Krause, M. J. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 135. (b) Vahrenkamp, H. *Adv. Organomet. Chem.* **1983**, *22*, 169. (c) Deeming, A. J. In *Transition Metal Clusters*; Johnson, B. F. G., Ed.; Wiley: New York, 1980; Chapter 5. (d) Muetterties, E. L.; Rhodin, T. N.; Band, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91. (e) Rofer-Deporter, C. K. *Chem. Rev.* **1981**, *81*, 447. (f) Gladfelter, W. L. *Adv. Organomet. Chem.* **1985**, *24*, 41.

(2) (a) Herman, R. G., Ed. *Catalytic Conversions of Synthesis Gas and Alcohols to Chemicals*; Plenum Press: New York, 1984, and references therein. (b) Moser, W. R., Ed. *Catalysis of Organic Reactions*; Marcel Dekker: New York, 1981, and references therein.

(3) (a) Fischer, F.; Tropsch, H. *Brennst.-Chem.* **1926**, *7*, 97. (b) Fischer, F.; Tropsch, H. *Chem. Ber.* **1926**, *59*, 830. (c) Brady, R. C.; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 6181. (d) Brady, R. C.; Pettit, R. *Ibid.* **1981**, *103*, 1287. (e) Sheldon R. A. *Chemicals from Synthesis Gas*; D. Reidel: Dordrecht, **1983**. (d) Henrici-Olive, G.; Olive, S. *The Chemistry of the Catalyzed Hydrogenation of Carbon Monoxide*; Springer-Verlag: New York, 1984.

it has been employed in catalytic studies of CO reduction.[5] Thus or principal objective is to generate formyl and acyl derivatives of the tetracobalt cluster I and to examine their chemical behavior. We proceeded in this study from an earlier brief report that the treatment of the tetracobalt cluster $Co_4(CO)_{10}(PPh)_2$ with a variety of hydridic reducing agents yielded the anionic hydride cluster $Co_4(CO)_9$-$(PPh)_2(\mu\text{-}H)^-$ in good yields.[6] However in mononuclear metal carbonyls, the favored attack by hydridic reagents occurs on the coordinated carbon monoxide to yield the corresponding formyl derivative.[7] The latter in many cases is converted to the hydridometal carbonyl in a separate, subsequent step.[8] Accordingly we reexamined the hydridic reduction of the tetracobalt cluster I under carefully controlled conditions. Parallel studies were also carried out on the susceptibility of the tetracobalt cluster to attack by carbanionic nucleophiles.

Results

I. Interaction of the Tetracobalt Cluster I with Borohydride. Formation of the Formyl Derivative.

When a clear red solution of $Co_4(CO)_{10}(PPh)_2$ (I) in tetrahydrofuran (THF) was mixed with 1 equiv of lithium triethylborohydride under an argon atmosphere at 25 °C, it immediately turned brown. Attendant upon this color change, the characteristic carbonyl stretching bands of I disappeared completely, and they were replaced by a different set at lower energy.[9] The new carbonyl bands were readily assigned to the hydrido species $Co_4(CO)_9$-$(PPh)_2(\mu\text{-}H)^-$ (II), which has been structurally characterized by Ryan and Dahl.[6] The bridging hydride ligand was detected as a high-field resonance at δ -13 in the ^1H NMR spectrum. The identical series of spectral changes were observed when the reducing agent was replaced by either potassium triisopropoxyborohydride or tri-*sec*-butylborohydride. We thus concluded that the cluster hydride II was a product that was common to the reduction of Co_4-$(CO)_{10}(PPh)_2$ by all of the borohydride reducing agents, i.e. eq 1, where X = CH_3CH_2, $(CH_3)_2CHO$, and $CH_3CH_2CHCH_3$.

$$Co_4(CO)_{10}(PPh)_2 + X_3BH^- \rightarrow$$

$$Co_4(CO)_9(PPh)_2H^- + CO + X_3B \quad (1)$$
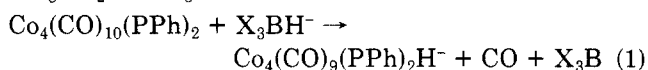
If the same reductions were carried out at -78 °C, the color change was more subtle. However, the inspection of the IR spectra of the reduced solution readily revealed a different set of carbonyl stretching bands. In particular, the lowest energy band at 1570 cm^{-1} was diagnostic of a formyl group that was bound to the tetracobalt cluster as a η^1 ligand.[7] The latter was confirmed by the ^{13}C NMR spectrum that showed the distinctive formyl resonance at δ 240 ($J_{H\text{-}C}$ = 150 Hz)[10] and by the low-field singlet resonance at δ 12.80 in the ^1H NMR spectrum.[11]

When the reducing agent was replaced by its deuterio derivative LiEt$_3$BD, the proton resonance at δ 12.80 was absent but reappeared in the ^2H NMR spectrum at the same chemical shift, consistent with the deuteriated functionality (-CDO). The IR and ^{13}C, ^1H, and ^2H NMR spectral changes were thus all consistent with an hydridic addition to a carbonyl ligand, i.e. eq 2. The resulting formyl cluster III persisted indefinitely at -78 °C.

$$Co_4(CO)_{10}(PPh)_2 + Et_3BH^2 \rightarrow$$
$$\text{I}$$

$$Co_4(CO)_9(PPh)_2C(O)H^- + Et_3B \quad (2)$$
$$\text{III}$$
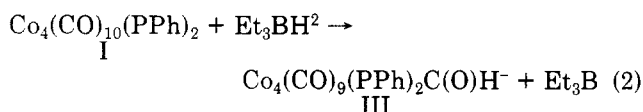
II. Spontaneous Decarbonylation of the Formyl Cluster III. Trapping by Alkylation at Low Temperatures.

The THF solutions of the formyl cluster III underwent little perceptible change as they were warmed to -25 °C. However beyond this temperature, the distinctive spectra began to disappear slowly—until the rate was rather rapid at 20 °C. The evolution of carbon monoxide resulted in a brown solution, the IR and ^1H NMR spectra of which were the same as that of the hydride cluster II. Thus the conversion of the formyl cluster to the hydride was complete, i.e. eq 3. The transient char-

$$Co_4(CO)_9(PPh)_2C(O)H^- \rightarrow Co_4(CO)_9(PPh)_2H^- + CO$$
$$\text{III} \qquad\qquad\qquad\qquad \text{II}$$
$$(3)$$
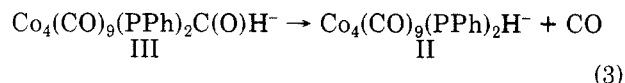
acter of the formyl cluster was thus consistent with it being the prime intermediate in the conversion of the tetracobalt cluster I to the μ-hydride, as in eq 1.

All attempts to retard the decarbonylation in eq 3, including the addition of active hydrogen atom donors such as tri-*n*-butyltin hydride, were unsuccessful.[12] Furthermore we were unable to isolate the anionic formyl cluster III as a crystalline salt at -78 °C. Accordingly we used two procedures to trap the anionic formyl cluster in situ and to convert it to a variety of neutral derivatives.

A. Addition of methyl trifluoromethanesulfonate (triflate) directly to the formyl cluster III in THF solution at -78 °C was accompanied by a color change from brown to red. The examination of the IR spectrum of the crude reaction mixture at this temperature showed that all the carbonyl stretching bands of III were shifted to higher energies.[13] This facile procedure for methylation was

(4) (a) Cardin, D. J.: Cetinkaya, B.; Doyle, M. J.; Lappert, M. F. *Chem. Soc. Rev.* **1973**, *2*, 99. (b) Herrman, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 160. (c) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479. (d) Knox, S. A. R. *Philos. Trans. R. Soc. London, Ser. A* **1982**, *308*, 67. (e) Casey, C. P.; Audett, J. D. *Chem. Rev.* **1986**, *86*, 339. (f) Shapley, J. R.; Sievert, A. C.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1981**, *103*, 6975. (g) Chisholm, M. H., Ed. *Reactivity of Metal-Metal Bonds*; ACS Symposium Series 155; American Chemical Society: Washington DC, **1981**; p 299. (h) Arce, A. J.; Deeming, A. J. *J. Chem. Soc., Chem. Commun.* **1982**, 364. (i) Schoening, R. C.; Vidal, J. L.; Fiato, R. A. *J. Mol. Catal.* **1981**, *13*, 83. (j) Curtis, M. D.; Messerle, L. *J. Am. Chem. Soc.* **1982**, *104*, 889. (k) Steinmetz, G. R.; Morrison, E. D.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 2559. (l) Morrison, E. D.; Steinmetz, G. R.; Geoffroy, G. L.; Fultz, W. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1984**, *106*, 4783.

(5) For studies dealing with the hydroformylation and hydrogenation activity of $Co_4(CO)_{10}(PPh)_2$, see: (a) Ryan, R. C.; Pittman, C. U.; O'Connor, J. P. *J. Am. Chem. Soc.* **1977**, *99*, 1986. (b) Pittman, C. U.; Wilemon, G. M.; Wilson, W. D.; Ryan, R. C. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 478. (c) Pittman, C. U.; Richmond, M. G.; Wilemon, G. M. Absi-Halabi, M. In *Catalysis of Organic Reactions*; Kosak, J. R., Ed.; Marcel Dekker: New York, 1984; Chapter 5. (d) Cf. also ref 6 and 9 for other physical studies pertaining to sundry other clusters derived from $Co_4(CO)_{10}(PPh)_2$.

(6) (a) Ryan, R. C. Ph.D. Thesis, University of Wisconsin—Madison, 1976. (b) Ryan, R. C.; Pittman, C. U.; O'Connor, J. P.; Dahl, L. F. *J. Organomet. Chem.* **1980**, *193*, 247.

(7) Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1.

(8) (a) Narayanan, B. A.; Amatore, C.; Casey, C. P.; Kochi, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 6351. (b) Narayanan, B. A.; Amatore, C. A.; Kochi, J. K. *Organometallics* **1984**, *3*, 802. (c) Narayanan, B. A.; Amatore, C. A.; Kochi, J. K. *Organometallics* **1986**, *5*, 926.

(9) Richmond, M. G.; Kochi, J. K. *Inorg. Chem.* **1986**, *25*, 1334.

(10) Metal formyl ^{13}C NMR resonances are typically observed from δ 220 to 310 with reported one-bond coupling constants $J_{H\text{-}C}$ ranging from ~120 to 150 Hz.[7]

(11) For examples of other cluster formyl complexes with low-field ^1H NMR chemical shifts, see: (a) Pruett, R. L.; Schoening, R. C.; Vidal, J. L.; Fiato, R. A. *J. Organomet. Chem.* **1979**, *182*, C57. (b) Johnson, B. F. G.; Kelly, R. L.; Lewis, J.; Thornback, J. R. *J. Organomet. Chem.* **1980**, *190*, C91. (c) Casey, C. P.; Neumann, S. M. *J. Am. Chem. Soc.* **1978**, *100*, 2544. (d) Tam, W.; Marsi, M.; Gladysz, J. A. *Inorg. Chem.* **1983**, *22*, 1413. (e) Steinmetz, G. R.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1981**, *103*, 1278. (f) Williams, G. D.; Geoffroy, G. L.; Whittle, R. R.; Rheingold, A. L. *J. Am. Chem. Soc.* **1985**, *107*, 729.

(12) For the effect of Bu_3SnH on the rate of decomposition of formyl complexes, see ref 8. These experiments utilized IR analysis to quantitatively assess the effect of Bu_3SnH on the rate of decomposition of III. For a description see Experimental Section.

found to be far superior to those employing either tri-methyloxonium tetrafluoroborate or methyl iodide as the alkylating agent, and it is thus related to the alkylation of anionic triosmium carbonyls previously reported by Kaesz and co-workers.[14] Thin-layer chromatographic (TLC) examination of the crude reaction mixture revealed the presence of two products in more or less equal amounts. Separation of the faster moving component by column chromatography led to red crystals of IV.


IV
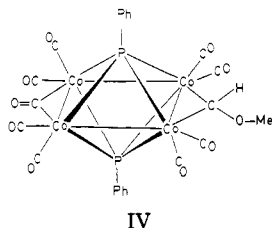
The limiting ^{13}C NMR spectrum of IV showed the μ-carbene ligand at δ 235 (J_{H-C} = 152 Hz) and one bridging carbonyl ligand at δ 239, together with resonances for terminal carbonyls at δ 204 (6 CO) and 202 (2 CO). This was consistent with the IR spectrum showing a single carbonyl stretching band for the bridging CO and multiple bands for the terminal carbonyls. Finally the ^{31}P NMR spectrum of IV revealed a classic AB quartet, as expected for inequivalent μ-phosphinidene caps. We recently showed this type of spectral resolution to be a useful probe for the structural delineation of the ancillary ligands about the cluster polyhedron.[15]

The slower-moving component V showed the principal features of the IR and ^{13}C (carbonyl) and ^{31}P NMR spectra to be similar to those of IV, which was indicative of an analogous structure shown in V. The latter formulation,


V
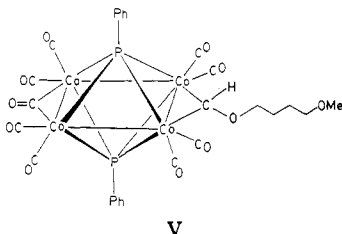
which derives from the cleavage of the ethereal solvent, was initially suggested from the ^1H NMR spectrum of V showing extensive resonances indicative of the THF residue. Thus the autocorrelated homonuclear (COSY)[16] ^1H NMR spectrum of V established the spin-coupling network inherent in the four-carbon methylene chain. The unequivocal evidence for the THF-derived methoxybutyl side chain in V was obtained from its ^{13}C NMR spectrum using spin-echo J-modulation spectroscopy[17] (see Experimental Section for the APT spectrum). The production of both the methyl as well as methoxybutyl derivatives IV and V relates to the alkylation of II directly by methyl triflate and by its THF-cleavage product, i.e. eq 4, which is also a powerful alkylating agent.[18,19]

$$CH_3O_3SCF_3 + \underset{}{\square}O \longrightarrow \underset{}{\square}\overset{+}{O}{-}CH_3^-O_3SCF_3 \quad (4)$$
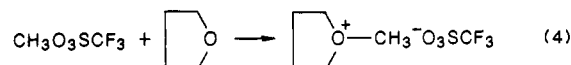
The formation of the bridged alkoxycarbene complexes IV and V by the trapping of the formyl intermediate III may be viewed in one of two ways. Thus O-alkylation of III can occur on the formyl ligand to yield the alkoxycarbene cluster $Co_4{=}CH(OCH_3)$, which then exchanges its terminal position with a bridged Co.[20] Alternatively the terminal formyl ligand in III may be in equilibrium with its bridged form, i.e. η^1-(O=CH)Co₄⁻ $\rightleftharpoons$ μ-(⁻O—CH=Co₄), which yields IV directly by methylation on oxygen.[21]

B. Addition of trifluoroacetic anhydride to a THF solution of the formyl cluster III led to a rapid reaction at −78 °C. Solvent removal in vacuo followed by extraction with hexane afforded a red solid in 62% yield. IR analysis indicated the formation of the trifluoroacetoxy adduct VI with only one μ-bridging carbonyl, the remainder of the carbonyl region resembling that of the methoxy derivative IV (see Experimental Section). These features, supported by the ^{31}P NMR spectrum with a pair of μ_4-phosphinidene resonances, indicated an analogous structure shown in VI. The methine proton of the bridging (trifluoroacetoxy)-carbene ligand in VI was observed as a doublet at δ 11.20 in the ^1H NMR spectrum.

VI
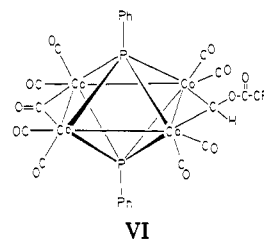
The formation of the two series of carbene complexes IV (V) and VI by trapping experiments carried at −78 °C with methyl triflate and trifluoroacetic anhydride demonstrates the intermediacy of a formyl cluster, III, attendant upon the reduction of $Co_4(CO)_{10}(PPh)_2$ by borohydrides, as in eq 1. More generally speaking, this intermediate represents the product of nucleophilic addition of an hydride moiety to the tetracobalt cluster I. As such, we turned our attention next to the reactivity of I toward the analogous carbon-centered nucleophiles.

III. Interaction of the Tetracobalt Cluster I with Carbanions. Formation of Carbene Derivatives. The tetracobalt cluster I reacted readily with methyllithium at −78 °C in much the same manner as it did with boro-

(13) (a) Fischer, E. O. *Angew. Chem.* 1974, *86*, 651. (b) Fischer, E. O. *Adv. Organomet. Chem.* 1976, *14*, 1.

(14) (a) Jensen, C. M.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* 1984, *106*, 5926. (b) Compare also: Fischer, E. O.; Offhaus, E. *Chem. Ber.* 1969, *102*, 2449. Casey, C. P.; Cyr, C. R.; Boggs, R. A. *Synth. Inorg. Met.-Org. Chem.* 1973, *3*, 249.

(15) Richmond, M. G.; Kochi, J. K. *Organometallics*, in press.

(16) (a) Bax, A.; Freeman, R. *J. Magn. Reson.* 1981, *42*, 164. (b) *Ibid.* 1981, *44*, 542.

(17) (a) Brown, D. W.; Nakashima, T. T.; Rabenstein, D. L. *J. Magn. Reson.* 1981, *45*, 302. (b) Jakobsen, H. J.; Sorensen, O. W.; Brey, W. S.; Kanyha, P. *J. Magn. Reson.* 1982, *48*, 328. (c) Rabenstein, D. L.; Nakashima, T. T. *Anal. Chem.* 1979, *51*, 1465A.

(18) For examples of THF cleavage by triflic acid and triflate esters, see: (a) Matyjaszewski, K.; Penczek, S. *J. Polym. Sci.* 1974, *12*, 1905. (b) Wu, T. K.; Pruckmayr, G. *Macromolecules* 1978, *8*, 77. (c) Kobayaski, S.; Danda, H.; Saegusa, T. *Macromolecules* 1974, *7*, 415. (d) Pruckmayr, G.; Wu, T. K. *Macromolecules* 1978, *11*, 265.

(19) (a) For reports of trans-alkylation products arising from methyl triflate and ether solvent exchange, see: Gramstad, T.; Haszeldine, R. N. *J. Chem. Soc.* 1956, 173 and ref 14a. (b) When THF was replaced with Et₂O as the solvent, the methoxy- and ethoxycarbene clusters were both observed in a 1:1 ratio upon workup.

(20) Such a transformation of a terminal carbene to a bridging carbene has been observed in other polynuclear systems. The driving force for such a process is presumably due to the greater stability associated with the μ-bridging carbene complex. For example, see: (a) Dyke, A. F.; Knox, S. A. R.; Mead, K. A.; Woodward, P. A. *J. Chem. Soc., Chem. Commun.* 1981, 861. (b) Laws, W. J.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* 1983, 1020. (c) Theopold, K. H.; Bergman, R. G. *J. Am. Chem. Soc.* 1983, *105*, 464. (d) Holmgren, J. S.; Shapley, J. R. *Organometallics* 1985, *4*, 793. (e) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* 1978, *17*, 800.

(21) However ^{13}C NMR measurements indicate that such an equilibrium lies entirely to the left. Within the limits of detection, it would not have been possible to observe 5% of the μ species; i.e., $K_{eq} < 0.05$.

hydride in eq 2. The analogous acetyl cluster VII formed by the nucleophilic addition of a methyl group to a coordinated CO, i.e. eq 5, was considerably more stable than

$$Co_4(CO)_{10}(PPh)_2 + CH_3Li \rightarrow$$
$$Co_4(CO)_9(PPh)_2C(O)CH_3^-Li^+ \quad (5)$$
$$VII$$

the formyl analogue III. Thus THF solutions of VII persisted for days even at 25 °C. The pattern of the carbonyl stretching bands in the IR spectrum of VII was similar to that of III—both sets being shifted to lower energies relative to that in the parent tetracobalt cluster I consistent with the increased electron density associated with these anionic clusters.[22] The acetyl band at 1574 cm⁻¹ was reminiscent of those present in other acetyl metalate complexes[23] and essentially the same as the formyl band in III. Furthermore the ¹³C NMR spectrum showed a low-field resonance at δ 291 consistent with the presence of an anionic acetyl derivative.[24] All attempts to isolate a single crystal of the acetyl salt VII suitable for X-ray crystallography were unsuccessful. Accordingly we again restored to the methylation and trifluoroacetoxylation procedures to convert the anionic acetyl cluster to various neutral derivatives.

A. Addition of methyl triflate to the acetyl cluster VII in THF solution led to a rapid reaction at –78 °C. TLC analysis indicated that two products were formed, and their subsequent separation by column chromatography afforded the pair of alkoxycarbene complexes VIII and IX,

VIII   IX
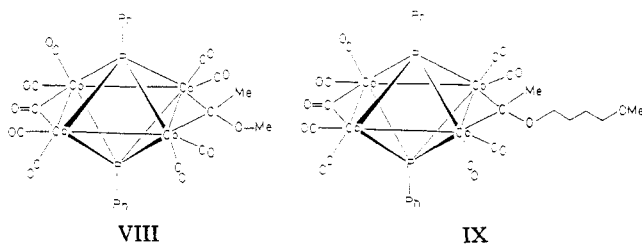
which were analogous to the pair (i.e. IV and V) generated via the formyl cluster III. Thus both VIII and IX displayed similar IR and ³¹P NMR spectra. The carbene complex IX was only distinguished from VIII on the basis of differences in their ¹H (COSY) and ¹³C NMR spectra as they related to the THF residue (see Experimental Section). Indeed the successful growth of a dark red single crystal allowed the unambiguous identification of the methoxymethylcarbene complex VIII (vide infra). This also served to establish the structure of the methoxycarbene cluster IV by comparison.

B. Addition of trifluoroacetic anhydride to a THF solution of the acetyl cluster VII led to a rapid reaction at –78 °C. The low-temperature IR spectrum was similar in the carbonyl region to that derived from the formyl cluster and formulated as VI. However when the reaction

Figure 1. 2D COSY ¹H NMR spectrum of $Co_4(CO)_9(PPh)_2[\mu\text{-}C=C(CH_2CH_2Me)H]$ in $CDCl_3$ at 25 °C.

mixture was worked up, a different cluster, X, was isolated and found to be devoid of the trifluoroacetoxy group. The single resonance at δ 180 in the ³¹P NMR spectrum of X was reminiscent of the singlet observed at δ 135 in the parent cluster I with idealized D_{2h} symmetry. The ¹H NMR spectrum of X revealed a singlet (2 H) resonance at δ 6.11 that integrated for two protons. The latter was unambiguously assigned to a vinylidene ligand from the ¹³C APT spectrum displaying a unique resonance at δ 126.9 with a positive intensity.[25] The formation of X can be readily accounted for by the elimination of trifluoroacetic acid from the first-formed (trifluoroacetoxy)carbene (compare the structure of VI) via the loss of the labile β-proton, i.e. eq 6. Indeed the successful isolation of a

X   (6)
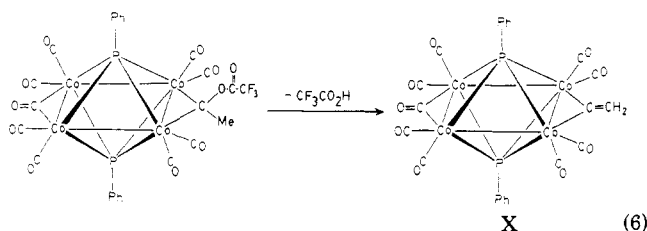
dark burgundy single crystal allowed the unambiguous identification of the vinylidene cluster X (vide infra).

In order to examine the generality of this interesting series of reactions, we treated $Co_4(CO)_{10}(PPh)_2$ first with

(22) Strong σ-donor ligands that are weak π-acceptors generally lower the stretching frequency of the ancillary CO ligands in metal carbonyl complexes. For discussions, see: (a) Shriver, D. F. *J. Organomet. Chem.* **1975**, *99*, 259. (b) Cotton, F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432. (c) Horwitz, C. P.; Shriver, D. F. *Adv. Organomet. Chem.* **1984**, *23*, 219. (d) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 3rd ed.; Wiley: New York, 1972; Chapter 22. (e) Purcell, K. F.; Kotz, J. C. *Inorganic Chemistry*; W. B. Saunders: Philadelphia, 1977; Chapter 18.

(23) (a) Collman, J. P.; Siegl, W. O. *J. Am. Chem. Soc.* **1972**, *94*, 2516. (b) Casey, C. P.; Meszaros, M. W.; Neumann, S. M.; Cesa, I. G.; Haller, K. J. *Organometallics* **1985**, *4*, 143 and references therein. (c) Collman, J. P.; Rothrock, R. K.; Finke, R. G.; Rose-Much, F. *J. Am. Chem. Soc.* **1977**, *99*, 7381. (d) Breen, M. J.; Shulman, P. M.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, W. C. *Organometallics* **1984**, *3*, 782.

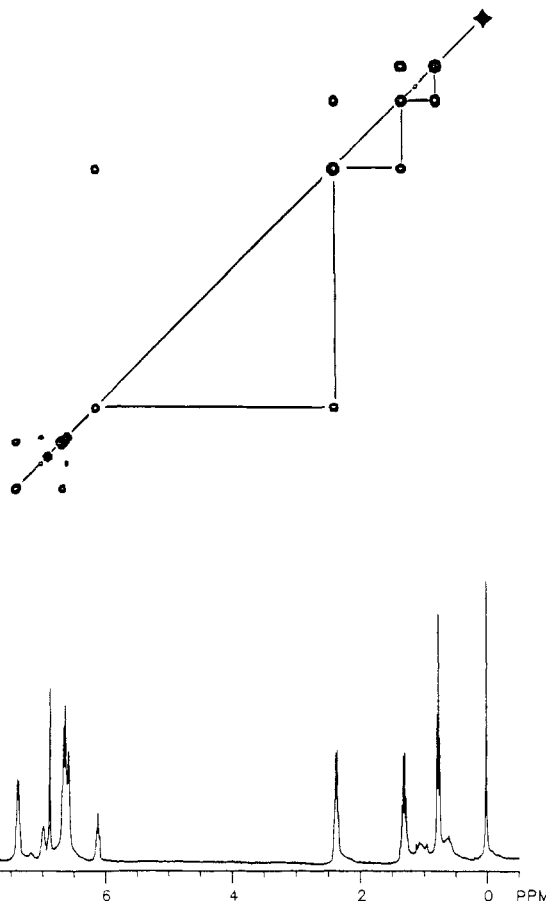(24) Mann, B. E.; Taylor, B. F. *¹³C NMR Data for Organometallic Compounds*; Academic Press: New York, 1981; pp 147–149.

(25) The reaction of trifluoroacetic anhydride with acyl anions possessing β-hydrogens is known to afford vinylidene complexes. See: (a) Boland, B. E.; Fam, S. A.; Hughes, R. P. *J. Organomet. Chem.* **1979**, *172*, C29. (b) Boland-Lussier, B. E.; Churchill, M. R.; Hughes, R. P.; Rheingold A. L. *Organometallics* **1982**, *1*, 628. (c) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59.
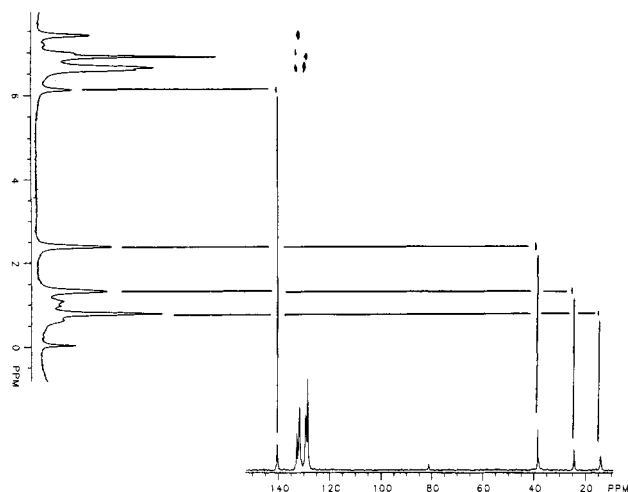
Figure 2. Proton-carbon 2D correlation spectrum of Co_4-$(CO)_9(PPh)_2[\mu$-C=C(CH_2CH_2Me)H]$ in $CDCl_3$ at 25 °C.

n-BuLi and then with trifluoroacetic anhydride in one operation. Workup of the reaction mixture afforded red crystals of XI in 60% yield. The IR spectrum of XI showed only one band at 1880 cm⁻¹ for a single bridging carbonyl; the ³¹P NMR spectrum displayed two resonances at δ 237 and 134 for a pair of inequivalent μ_4-phosphinidenes. Both spectral methods supported a cluster with the structure shown in XI. Indeed the presence of the

XI
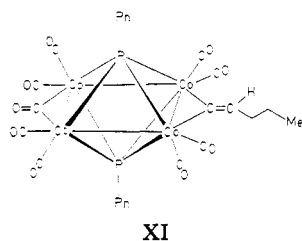
n-propyl side chain in XI was established from its well-resolved ¹H NMR spectrum with the methyl resonance at δ 0.76, the methylenes at δ 1.30 and 2.38, and the methine at δ 6.12. Further structure proof for the existence of the propylvinylidene group (=CHCH₂CH₂CH₃) was demonstrated by multiple-resonance NMR techniques. For example, the ¹H COSY spectrum of XI is shown in Figure 1 with the off-diagonal spin-coupling networks serving to illustrate the proton–proton connectivity. Thus the lone vinyl proton (H_a) at δ 6.11 correlated with the adjacent γ-methylene (H_b) at δ 2.38, which showed a correlation to the γ-methylene (H_c) at δ 1.30. The last response correlated with the ε-methyl (H_d) at δ 0.79. The presence of the four-spin-coupling network for H_a–H_d established this system as arising from the *n*-butyllithium reducing agent. Furthermore the ¹³C APT spectrum of XI revealed the identities of the resonances arising from the γ- and δ-methylene as well as the ε-methyl carbons but not that of the β-vinylidene carbon (owing to its similar response with those of the aromatic carbons). Therefore the unambiguous assignment of the ¹³C resonance of the β-methine carbon was based on the heteronuclear ¹H–¹³C chemical shift correlation spectrum shown in Figure 2, which provided direct ¹H–¹³C connectivities.[26] Thus from the known ¹H chemical shift of the methine proton at δ 6.11, the low-field ¹³C resonance at δ 140 was readily assigned to the β-vinylidene carbon. Moreover, the three high-field ¹³C

Table I. X-ray Crystallographic Data for the Carbene Derivatives of Tetracobalt Clusters
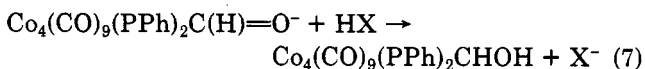
	$Co_4(CO)_9(PPh)_2$-$[\mu$-C(OMe)Me]$	$Co_4(CO)_9(PPh)_2$-$(\mu$-C=CH_2)$
space group	$P2_1/c$, monoclinic	$P2_1/n$, monoclinic
cell constants		
a, Å	16.465 (2)	9.954 (1)
b, Å	23.987 (3)	12.865 (3)
c, Å	15.775 (2)	10.270 (1)
β, deg	112.61 (1)	98.88 (1)
V, Å³	5752	1299
mol formula	$C_{24}H_{16}Co_4P_2O_{10}$	$C_{23}H_{12}Co_4P_2O_9$
fw	762.14	730.0
formula units per cell (Z)	8	2
ρ, g cm⁻³	1.76	1.87
abs coeff (μ), cm⁻¹	24.25	26.77
radiatn (λ), Å	Mo Kα (0.710 73)	Mo Kα (0.710 73)
collectn range, deg	$4 \leq 2\theta \leq 35$	$4 \leq 2\theta \leq 50$
scan width ($\Delta\theta$), deg	1.00 + 0.35 tan θ	0.90 + 0.35 tan θ
max scan time, s	150	120
scan speed range, deg min⁻¹	0.6–5.0	0.7–5.0
total data collected	3462	2535
independent data, $I > 3\sigma(I)$	1819	1953
total variables	381	170
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.051	0.025
$R_w = [\sum w(\|F_o\| - \|F_c\|)^2/\sum w\|F_o\|^2]^{1/2}$	0.046	0.030
weights	$w = \sigma(F)^{-2}$	$w = \sigma(F)^{-2}$

resonances at δ 14, 24, and 38 arose from the methyl and δ- and γ-methylene carbons, respectively, of the *n*-propyl side chain.

IV. X-ray Crystallography of the Carbene Derivatives of Tetracobalt Clusters. The disposition of the ancillary ligands in the saturated and unsaturated carbene derivatives VIII and X, respectively, of the tetracobalt cluster was determined by single-crystal X-ray crystallography. The collection data and processing data for $Co_4(CO)_9(PPh)_2[\mu$-C(OMe)Me]$ (VIII) and $Co_4(CO)_9$-$(PPH)_2(\mu$-C=CH_2)$ (X) are presented in Table I, and the ORTEP diagrams are illustrated in Figure 1.

Each of the carbene clusters was comprised of four cobalt atoms in a rectangular array whose shorter sides were bridged on one side by a bridging carbonyl and on the other side by the μ-carbene ligand. The capping of the cobalt tetramer by a pair of μ_4-phenylphosphinidenes completed the overall octahedral Co_4P_2 core common to this genre of cluster.[6,9,15] Indeed the structural parameters of both clusters VIII and X were essentially the same except in the vicinity of the carbene ligands, as given by the listing of the principal bond distances and angles in Tables II and III.

V. Reactivity of the Formyl Cluster II as a Hydrogen Donor. We initially examined the protonation of the anionic formyl cluster III as a possible route to the hydroxycarbene derivative, i.e. since such species are potential intermediates in the reduction of coordinated CO.[27] When trifluoroacetic acid (HX) was added slowly under an argon atmosphere to the formyl cluster III at -60 °C, the brown THF solution immediately reverted to red. Attendant upon this color change, the characteristic car-
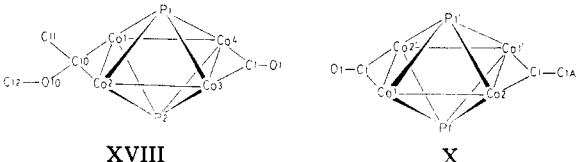
$$Co_4(CO)_9(PPh)_2C(H)=O^- + HX \rightarrow$$
$$Co_4(CO)_9(PPh)_2CHOH + X^- \quad (7)$$

(26) (a) Maudsley, A. A.; Muller, L.; Ernst, R. R. *J. Magn. Reson.* **1977**, *28*, 463. (b) Bodenhausen, G.; Freeman, R. *J. Magn. Reson.* **1977**, *28*, 471. (c) *J. Am. Chem. Soc.* **1978**, *100*, 320.

(27) (a) Casey, C. P.; Neumann, S. M. Andrews, M. A.; McAlister, D. R. *Pure Appl. Chem.* **1980**, *52*, 625. (b) Demitras, G. C.; Muetterties, E. L. *J. Am. Chem. Soc.* **1977**, *99*, 2796. (c) Wender, I. *Catal. Rev.—Sci. Eng.* **1976**, *14*, 97. (d) Blackborow, J. R. Daroda, R. J.; Wilkinson, G. *Coord. Chem. Rev.* **1982**, *43*, 17. (e) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61.

Table II. Selected Bond Lengths (Å) in the Carbene Clusters Co₄(CO)₉(PPh)₂[μ-C(OMe)Me] (VIII) and Co₄(CO)₉(PPh)₂[μ-C=CH₂] (X)ᵃ

Table II. Selected Bond Lengths (Å) in the Carbene Clusters $Co_4(CO)_9(PPh)_2[\mu\text{-}C(OMe)Me]$ (VIII) and $Co_4(CO)_9(PPh)_2[\mu\text{-}C{=}CH_2]$ (X)[a]

XVIII   X

| A–B	VIII[b]	X
Co(1)–Co(2)	2.500 (3)	2.717 (1)
Co(1)–Co(2′)		2.504 (1)
Co(2)–Co(3)	2.701 (3)	
Co(3)–Co(4)	2.510 (3)	
Co(4)–Co(1)	2.709 (3)	
Co(1)–C(10)	2.034 (14)	
Co(2)–C(10)	2.026 (14)	
Co(3)–C(1)	1.89 (2)	
Co(4)–C(1)	1.92 (2)	
Co(1)–C(1)		1.927 (2)
C(2)–C(1)		1.928 (2)
C(1)–O(1)	1.20 (2)	1.217 (4)
C(1)–C(1A)		1.355 (6)
C(10)–C(11)	1.55 (2)	
C(10)–O(10)	1.384 (15)	
O(10)–C(12)	1.45 (2)	
P(1)···P(2)	2.534 (5)	
P(1)···P(1′)		2.543 (1)

ᵃ The number in parentheses is the estimated standard deviation in the least significant digit. ᵇ Bond distances represent average values for the two observed crystallographically independent molecules.

Table III. Principal Bond Angles (deg) in the Carbene Clusters Co₄(CO)₉(PPh)₂[μ-C(OMe)Me] (VIII) and Co₄(CO)₉(PPh)₂(μ-C=CH₂) (X)ᵃ

Table III. Principal Bond Angles (deg) in the Carbene Clusters $Co_4(CO)_9(PPh)_2[\mu\text{-}C(OMe)Me]$ (VIII) and $Co_4(CO)_9(PPh)_2(\mu\text{-}C{=}CH_2)$ (X)[a]

A–B–C	VIII[b]	X
Co(2)–Co(1)–Co(4)	90.28 (9)	
Co(1)–Co(2)–Co(3)	89.95 (9)	
Co(1)–Co(2)–Co(1′)		90.28 (1)
Co(2)–Co(1′)–Co(2′)		89.72 (1)
Co(1)–P(1)–Co(2)	68.1 (2)	74.54 (1)
Co(1)–P(1)–Co(4)	74.6 (2)	
Co(1)–P(1)–Co(2′)		67.69 (1)
Co(1)–C(1)–Co(2′)		80.99 (6)
Co(1)–C(10)–Co(2)	76.0 (5)	
Co(3)–C(1)–Co(4)	82.7 (7)	
Co(11)–C(10)–O(10)	113.5 (20)	
C(12)–O(10)–C(10)	123.5 (10)	

ᵃ For numbering scheme, see Table II. Numbers in parentheses are estimated standard deviations in the least significant digit. ᵇ Bond angles represent average values for the two observed crystallographically independent molecules.

bonyl stretching bands of the parent tetracobalt cluster I reappeared at 2041, 2029, 2015, and 1871 cm⁻¹. We judged from their intensity that $Co_4(CO)_{10}(PPh)_2$ was a major product (>85%). Indeed, its separation by column chromatography confirmed the re-formation of the parent cluster as a result of protonation, i.e. eq 8. The 1:1

$$Co_4(CO)_9(PPh)_2CHO^- + CF_3CO_2H \rightarrow$$
$$\text{III}$$
$$Co_4(CO)_{10}(PPh)_2 + H_2 + CF_3CO_2^- \quad (8)$$
$$\text{I}$$
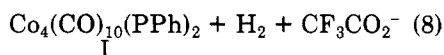
stoichiometry in eq 7 suggests that hydrogen was a by-product, but its identity was not confirmed. GC–MS analysis of the organic products failed to detect form-aldehyde, methanol, or methane.

The acidification of the formyl cluster III in eq 8 for-mally represents the transfer of a hydridic moiety to a proton. As such, we next examined its ability to donate

hydride to a metal carbonyl. Accordingly the formyl cluster III was generated in tetrahydrofuran and then treated with an equimolar amount of iron pentacarbonyl at –60 °C. After the mixture was allowed to warm grad-ually to room temperature, inspection of the ¹H NMR spectrum indicated a shift of the low-field formyl proton completely to a new resonance at δ 14.26. The latter co-incided with that of the formyl iron species $Fe(CO)_4CH\text{-}O^-$.[28] This assignment was supported by IR analysis of the formyl band at 1559 cm⁻¹, and it was confirmed by deuterium-labeling studies (see Experimental Section). The major cobalt-containing product was the parent cluster I contaminated with minor amounts (>10%) of the μ-hydride. Accordingly we formulate the overall trans-formation as eq 9. The path for such a transformylation

$$Co_4(CO)_9(PPh)_2CHO^- + Fe(CO)_5 \rightarrow$$
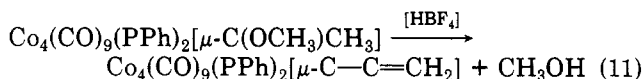$$Co_4(CO)_{10}(PPh)_2 + Fe(CO)_4CHO^- \quad (9)$$
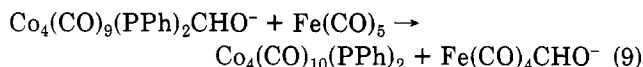
could involve a two-step process in which the prior de-composition of the formyl cluster as in eq 3 is followed by hydride transfer. This possibility is unlikely since in separate experiments we could find no reaction between the hydride cluster $Co_4(CO)_9(PPh)_2H^-$ and iron penta-carbonyl. We thus conclude that the transformylation in eq 9 derives from the ability of the formyl cluster III to act directly as a reagent for hydride donation.[29]

VI. Alternate Route to Vinylidene Clusters.
Fischer-type carbenes are known to afford vinylidene metal complexes by a proton-induced elimination of alcohol (ROH), e.g.[30] eq 10. The ease with which such transfor-

$$M{-}CH \xrightarrow{[HX]} MCH{=}CH_2 + ROH \quad (10)$$
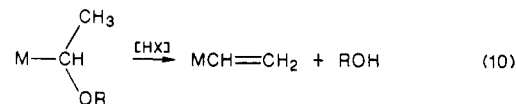
mations occur is doubtlessly related to the stabilization of the carbocationic center $M\text{-}C^+HCH_3$ formed by the protonation of the alkoxy group and subsequent loss of alcohol.[31] To determine whether the tetracobalt core is capable of inducing a similar effect, i.e. eq 11, we treated

$$Co_4(CO)_9(PPh)_2[\mu\text{-}C(OCH_3)CH_3] \xrightarrow{[HBF_4]}$$
$$Co_4(CO)_9(PPh)_2[\mu\text{-}C{-}C{=}CH_2] + CH_3OH \quad (11)$$

the carbene cluster VIII in toluene with tetrafluoroboric acid at –78 °C. No reaction was apparent until the tem-perature of the reaction mixture was allowed to rise to 25 °C. The ¹H and ³¹P NMR examination indicated that the

(28) For the IR and ¹H NMR spectroscopic properties of Fe(CO)₄CH-O⁻, see: (a) Collman, J. P.; Winter, S. R. *J. Am. Chem. Soc.* **1973**, *95*, 4089. (b) Winter, S. R.; Cornett, G. W.; Thompson, E. A. *J. Organomet. Chem.* **1977**, *133*, 339. (c) Reference 23a.

(29) Iron pentacarbonyl has been transformylated by a variety of other formylmetals acting as hydride donors. This contrasts with a pathway involving formyl transfer or transfer of a hydride derived from the de-composition of a formylmetal. See: (a) Casey, C. P.; Newmann, S. M. *Adv. Chem. Ser.* **1979**, *No. 173*, 132. (b) Gladysz, J. A.; Tam, W. *J. Am. Chem. Soc.* **1978**, *100*, 2545. (c) Gladysz, J. A.; Williams, G. M.; Tam, W.; Johnson, D. L. *J. Organomet. Chem.* **1977**, *140*, C1.

(30) For analogous processes in mononuclear organometallic com-plexes, see: (a) Pearson, A. J. *Metallo-organic Chemistry*; Wiley: New York, 1985; Chapter 4. (b) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980; Chapter 3. (c) Dotz, K. H.; Fischer, H.; Hoffmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1983.

(31) (a) Casey, C. P.; Fagan, P. J.; Miles, W. H.; Marder, S. R. *J. Mol. Catal.* **1983**, *21*, 173. (b) Casey, C. P.; Marder, S. R.; Rheingold, A. L. *Organometallics* **1985**, *4*, 762. (c) Casey, C. P.; Meszaros, M. W.; Fagan, P. J.; Bly, R. K.; Marder, S. R.; Austin, E. A. *J. Am. Chem. Soc.* **1986**, *108*, 4043. (d) Casey, C. P.; Meszaros, M. W.; Fagan, P. J.; Bly, R. K.; Colburn, R. E. *J. Am. Chem. Soc.* **1986**, *108*, 4053.

vinylidene derivative X was present in only ~25% yield, together with unidentified material (see Experimental Section).

VII. Attempted Carbene Transfer from Tetracobalt Clusters.

The reactivity of organometallic carbene complexes in the cyclopropanation of olefins is known.[32] Accordingly we examined the ability of Co$_4$(CO)$_9$(PPh)$_2$-[μ-C(OMe)CH$_3$] (VIII) to transfer its carbene ligand to an olefin. The exposure of VIII to neat cyclohexene at 120 °C in a sealed tube led only to a slow reaction. Analysis of the reaction mixture indicated that the parent Co$_4$-(CO)$_{10}$(PPh)$_2$ was regenerated in high yields (~75% by IR analysis). However we found no evidence for organic products derived from cyclohexene. The fate of the methoxymethylcarbene moiety was not ascertained. When the reaction was repeated under an atmosphere of carbon monoxide (120 psi) in a Fisher-Porter pressure vessel, no decomposition of VIII was observed, even after prolonged heating. This suggested that the decomposition of the carbene complex was preceded by the dissociative loss of CO, and it is under further investigation.

Discussion

The reduction of the tetracobalt cluster Co$_4$(CO)$_{10}$(PPh)$_2$ by borohydride reducing agents is shown to proceed via the metastable formyl intermediate III that is identified by its low-temperature IR spectrum as well as by its distinctive ^{1}H, ^{2}H, and ^{13}C NMR spectra. The formyl cluster is most likely derived by hydridic attack on a terminal CO and not at a carbonyl in a bridging position.[33] The carbonyl stretching frequency at low energy (1570 cm^{-1}) in the IR spectrum of III together with the ^{13}C resonance at low field (δ 240) in the NMR spectrum suggests the presence of a relatively large amount of negative charge on the formyl oxygen, as illustrated in IIIB. The facile O-alkylations and O-trifluoroacylation of the formyl cluster III and its acetyl analogue VII are manifestations of this nucleophilic oxygen center.[34]

IIIA　　　　　　　　　　IIIB
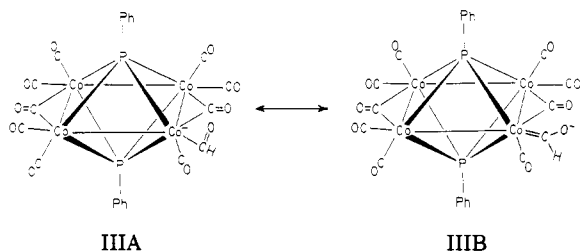
The formyl cluster III is thermally unstable at temperatures above −20 °C and decomposes cleanly to hydride cluster Co$_4$(CO)$_9$(PPh)$_2$(M-H)$^-$ (II). A free radical chain

Scheme I
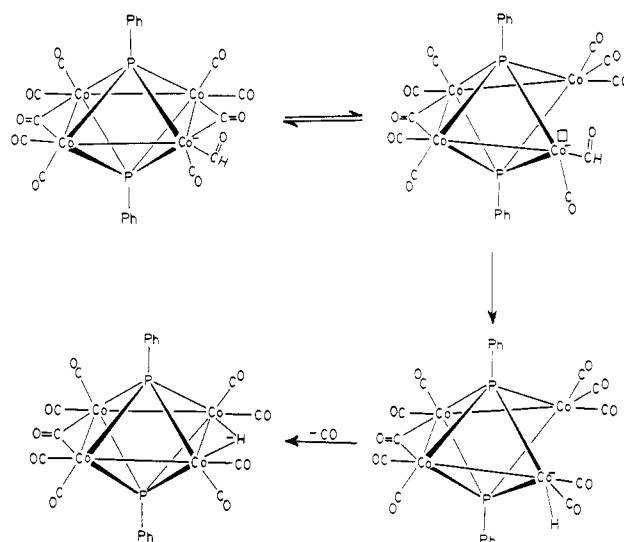
mechanism has been shown to participate in similar transformations of a number of formylmetals.[8] However the absence of inhibition by Bu$_3$SnH does not support the participation of such a pathway for the formyl cluster III. A molecular mechanism may involve a prior dissociative loss of CO from the cobalt center bound to the formyl group.[35] The migratory deinsertion of CO from such a coordinatively unsaturated site has been presented.[36] An alternative mechanism relies on the scission of the Co–Co bond in the cluster to generate a coordinatively unsaturated Co site capable of allowing the carbonyl deinsertion of a bound formyl group. Such a facile ring opening of the tetracobalt core has been suggested as a key step in the ligand substitution in this genre of cluster.[9,37] Furthermore the viability of Co–Co bond scission is supported by the polyhedral skeletal electron pair (PSEP) formalism,[39] as illustrated in Scheme I.

The initial six-vertex closo structure III possesses eight skeletal electron pairs (SEP), which is one more than predicted.[40] With this electron count, the conversion of the closo structure III to the favored nido structure III' generates a vacant coordination site on a cluster with an unchanged SEP count. Migratory deinsertion of the formyl group attached at the site of unsaturation would afford a terminal hydride in a nido cluster possessing nine SEPs. The subsequent, rapid dissociative loss of CO is then

(32) (a) Jolly, P. W.; Pettit, R. *J. Am. Chem. Soc.* **1966**, *88*, 5044. (b) Davison, A.; Krusell, W.; Michaelson, R. *J. Organomet. Chem.* **1974**, *72*, C7. (c) Casey, C. P.; Miles, W. H. *Organometallics* **1984**, *3*, 808. (d) Brookhart, M.; Kegley, S. E.; Husk, G. R. *Organometallics* **1984**, *3*, 650. (d) Wulff, W. D.; Kaesler, R. W. *Organometallics* **1985**, *4*, 1461. (e) Helquist, P.; Brandt, S. *J. Am. Chem. Soc.* **1979**, *101*, 6473. (f) Casey, C. P. In *Reactive Intermediates*; Wiley, New York, 1985; Vol 2, Chapter 4.

(33) This possibility is supported by both experimental and theoretical work. For example, see: (a) Harris, M. M.; Atwood, J. D.; Wright, M. E.; Nelson, G. O. *Inorg. Chem.* **1982**, *21*, 2117. (b) Jemmis, E. D.; Pinhas, A. R.; Hoffman, R. *J. Am. Chem. Soc.* **1980**, *102*, 2576. (c) Dedieu, A.; Nakamura, S. *Nouv. J. Chim.* **1984**, *8*, 317. (d) Albright, T. A., personal communication.

(34) (a) Wong, W.; Chiu, K. W.; Wilkinson, G.; Galas, A. M. R.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1983**, 1557. (b) Gavens, P. D.; Mays, M. J. *J. Organomet. Chem.* **1978**, *162*, 389. (c) Keister, J. B. *J. Organomet. Chem.* **1980**, *190*, C36. (d) Horwitz, C. P.; Holt, E. M.; Shriver, D. F. *Inorg. Chem.* **1984**, *23*, 2491. (e) Whitmire, K. H.; Shriver, D. F. *J. Am. Chem. Soc.* **1981**, *103*, 6754. (f) Whitmire, K.; Shriver, D. F. *J. Am. Chem. Soc.* **1980**, *102*, 1456.

(35) For examples of enhanced ligand lability in anionic organometallic cluster compounds, see: (a) Darensbourg, D. J.; Gray, R. L.; Pala, M. *Organometallics* **1984**, *3*, 1928. (b) Anstock, M.; Taube, D.; Gross, D. C.; Ford, P. C. *J. Am. Chem. Soc.* **1984**, *106*, 3696. (c) Lavigne, G.; Kaesz, H. D. *J. Am. Chem. Soc.* **1984**, *106*, 4647.

(36) (a) Gladysz, J. A.; Selover, J. C. *Tetrahedron Lett.* **1978**, 319. (b) Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Jones, W. D.; Harsy, S. G. *J. Mol. Catal.* **1981**, *13*, 43. (c) Smith, G.; Cole-Hamilton, D. J. *J. Chem. Soc., Dalton Trans.* **1984**, 1203. (d) Tam, W.; Lin, G. Y.; Gladysz, J. A. *Organometallics* **1982**, *1*, 525. (e) Wojcicki, A. *Adv. Organomet. Chem.* **1973**, *11*, 87. (f) Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299. (g) Davies, S. G.; Simpson, S. J. *J. Organomet. Chem.* **1984**, *268*, C53.

(37) (a) Richmond, M. G.; Korp, J. D.; Kochi, J. K. *J. Chem. Soc., Chem. Commun.* **1985**, 1102. (b) See also ref 38.

(38) (a) Hieber, W.; Kruck, T. *Chem. Ber.* **1962**, *95*, 2027. (b) Bogan, L. E.; Lesch, D. A.; Rauchfuss, T. B. *J. Organomet. Chem.* **1983**, *250*, 429.

(39) (a) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1. (b) Wade, K. In *Transition Metal Clusters*; Johnson, B. F. G., Ed.; Wiley: New York, 1980; Chapter 3. (c) Mingos, D. M. P. *Adv. Organomet. Chem.* **1977**, *15*, 1. (d) Mingos, D. M. P. *Nature (London), Phys. Sci.* **1976**, *9*, 446.

(40) The possibility of accommodating eight SEP in the tetracobalt cluster[41] does not materially effect the following argument.[42]

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followed by the re-formation of the Co–Co bond and the migration of hydride to the bridging position in II.

We propose that the acetyl analogue VII has the same overall structure as the formyl cluster III on the basis of spectral similarities. Thus the limiting ^{13}C NMR spectrum displays two distinct μ-CO resonances at δ 247 and 236. The low-field ^{13}C resonance at δ 291 together with the low-energy IR band at 1574 cm^{-1} for the acetyl group suggests a high degree of negative charge delocalized onto the oxygen atom as in IIIB (vide supra). The acetyl cluster VII is substantially more persistent than the formyl cluster which may be related to the relative ease of migratory deinsertion of formyl and acetyl groups (compare Scheme I).

The acyl clusters III and VII are efficiently converted to the methoxycarbene derivatives IV and VIII, respectively with methyl triflate. These methylations probably arise by O-alkylation of the η^1-acyl ligands to initially afford the terminal carbene intermediate that rearranges to the μ-carbene cluster during isolation.[43]

The trifluoroacetylation of III is analogous to methylation. With VII however, the (trifluoroacetoxy)carbene intermediate is unstable and spontaneously loses trifluoroacetic acid to furnish the μ_2-vinylidene derivative X. The latter is also achieved by an acid-catalyzed elimination of methanol from the methoxycarbene cluster IV.

The utility of this synthesis of vinylidene clusters was extended to alkyl derivatives such as XI. The transformation was readily achieved in a one-pot process in which alkyllithium and trifluoroacetic anhydride were serially added to the parent cluster Co$_4$(CO)$_{10}$(PPh)$_2$. Multiple-resonance NMR techniques including COSY, APT, and heteronuclear correlation provided the unequivocal and facile assignment of the structural details of the vinylidene ligand. We hope that these synthetic routes will provide facile entries into a variety of other vinylidene clusters.[44]

Experimental Section

General Data. All reactions were carried out under an atmosphere of dry argon by using Schlenk techniques.[45] Tetrahydrofuran, 2-methyltetrahydrofuran, diethyl ether, benzene, and toluene were distilled from sodiobenzophenone prior to use. Deuteriated solvents were degassed by successive freeze–pump–thaw cycles and used without further purification. Methyl trifluoromethanesulfonate was prepared according to the published procedure.[46] LiEt$_3$BH (1.0 M in THF) and MeLi (0.5 M in Et$_2$O) were used as received (Aldrich). The latter was titrated against diphenylacetic acid prior to use.[47] Trifluoroacetic anhydride was prepared by the dehydration of trifluoroacetic acid with P$_2$O$_5$. Co$_4$(CO)$_{10}$(PPh)$_2$ and the ^{13}CO-enriched cluster were prepared by using published procedures.[9] All reported ^{13}C NMR data in the metal carbonyl region (δ 180–300) utilized ^{13}CO-enriched Co$_4$(CO)$_{10}$(PPh)$_2$ with added Cr(acac)$_3$ ($\sim$0.7 mol %) as a shiftless relaxation agent.[48] Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, GA.

Instrumentation. Infrared spectra were recorded on a Nicolet 10-DX FT spectrometer in either 0.1- or 1.0-mm NaCl cells. The ^{31}P (36.2-MHz), ^{1}H (89.5-MHz), and ^{13}C (22.5-MHz) NMR spectra were recorded on a JEOL FX-90Q spectrometer. The ^{1}H

(300.1-MHz) and ^{13}C (75.5-MHz) NMR spectra were recorded on a Nicolet NT-300 wide-bore spectrometer. All J_{H-C} coupling constants reported for the ^{13}C NMR data were obtained under gated decoupling conditions with NOE enhancement. ^{1}H and ^{13}C NMR data are referred to Me$_4$Si, while the ^{31}P NMR data are referred to external 85% H$_3$PO$_4$. Positive chemical shifts are to low field of the external standard. The NT-300 spectrometer was equipped with a Nicolet Model 293C pulse programmer and a 5-mm dual-tuned ^{1}H/^{13}C probe. For all multiple-resonance experiments, the 90° ^{13}C observed pulse was calibrated as 17.5 μs by using the two-dimensional pulse calibration procedure described by Lawn and Jones.[49] The 90° ^{1}H pulse from the decoupler was calibrated as 27.5 μs by taking $^1/_4(\gamma H/2\pi)$.

Autocorrelated Two-Dimensional ^{1}H NMR (COSY) Spectra. All COSY spectra were acquired by using the standard 90°–t_1–90° acquire pulse sequence,[16a] with the initial $\mathbf{S}(t_1,t_2)$ data matrix consisting of 1024 × 512 data points to yield a 512 × 512 $\mathbf{F}_1\mathbf{F}_2$ data matrix that was symmetrized to enhance signal-to-noise. The data acquired after the 90° read pulse was phase cycled to provide the equivalent of quadrature detection in both time domains. The data presented in Figure 1 are shown as a seven-level contour plot.

Heteronuclear Proton–Carbon Chemical Shift Correlation. The heteronuclear chemical shift correlation spectrum in Figure 2 was acquired by using the pulse sequence of Freeman and Morris,[50] modified to provide quadrature detection in the second frequency domain as described by Bax and Morris.[51] The data was acquired as a 256 × 1K matrix (140 blocks of 256 were acquired) to yield a 256 × 256 $\mathbf{F}_1\mathbf{F}_2$ data matrix that was processed by using a 1.0-Hz exponential broadening prior to the first Fourier transformation and a double-exponential apodization prior to the second Fourier transformation.

Attached Proton Test (APT). This *J*-modulation spin-echo experiment utilized the standard PD–45°–D1–180°–D1–180°–D6 pulse seqeunce that is equipped with the NT-300 spectrometer. The broad-band proton decoupler was gated off during the first D1 delay and then back on for data collection. All spectra were obtained employing quadurature phase detection and automatic base line collect 180° phase shifts to remove DC bias between the two receiver channels.

Reaction of Co$_4$(CO)$_{10}$(PPh)$_2$ with Triethylborohydride. To 0.25 g (0.34 mmol) of Co$_4$(CO)$_{10}$(PPh)$_2$ in 20 mL of THF at –78 °C was added 0.35 mL of 1.0 M LiEt$_3$BH. The color of the reaction turned from red to dark red-brown, indicating the formation of the anionic formyl cluster. The formyl cluster was not isolated since it decomposes above –20 °C to the known anionic μ-hydride [Co$_4$(CO)$_9$(PPh)$_2$(μ-H)]Li. However, the identity of the formyl cluster was ascertained from its spectral properties and subsequent conversion to derivatized products (vide supra). IR (THF, sampled at –78 °C): ν_{CO} 2041 (w), 2005 (vs), 1991 (s), 1976 (s), 1849 (m), 1570 (w, formyl C=O) cm^{-1}. ^{31}P{^{1}H} NMR (THF/benzene-d_6, 4:1 v/v; –50 °C): δ 135 (b s). ^{13}C{^{1}H} NMR (2-methyltetrahydrofuran/benzene-d_6, 4:1 v/v; –90 °C): δ 247.0 (1, μ-carbonyl), 240.1 (1, formyl C=O, J_{H-C} = 150 Hz), 219.0 (1, μ-carbonyl), 205.0 (7, b, terminal carbonyls). ^{1}H NMR (THF/benzene-d_6, 4:1 v/v; –50 °C) δ 12.80 (1, formyl). Yield: >50% (vide infra).

Reaction of Co$_4$(CO)$_{10}$(PPh)$_2$ with Methyllithium. To 0.15 g (0.20 mmol) of Co$_4$(CO)$_{10}$(PPh)$_2$ in 8 mL of THF at –78 °C was added 0.5 mL of 0.5 M MeLi. The reaction with MeLi was instantaneous, and the anionic acetyl cluster was characterized by its spectral properties and subsequent conversion to derivatized products. IR (THF, 25 °C): ν_{CO} 2039 (m), 2000 (vs), 1988 (s), 1979 (s), 1961 (sh), 1840 (m, b), 1574 (w, acetyl C=O) cm^{-1}. ^{13}C{^{1}H} NMR (2-methyltetrahydrofuran/benzene-d_6, 4:1 v/v; –90 °C): δ 291.4 (1, acetyl C=O), 247.0 (1, μ-carbonyl), 236.0 (1, μ-carbonyl), 205.0 (7, b, terminal carbonyls). Yield: >60% (vide infra).

Reaction of Co$_4$(CO)$_9$(PPh)$_2$CHO$^-$Li$^+$ with Methyl Triflate. To a 50-mL THF solution containing 0.79 mmol of III at –78 °C was added 0.09 mL (0.80 mmol) of MeOSO$_2$CF$_3$. Stirring was continued for 2.0 h at –78 °C. The reaction mixture was then

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concentrated to dryness in vacuo. TLC examination (hexane/benzene, 8:2 v/v) of the crude reaction material revealed the presence of two products. These products were isolated by column chromatography and subsequently identified as $Co_4(CO)_9$-$(PPh)_2[\mu\text{-}C(OMe)H]$ (faster moving product) and $Co_4(CO)_9$-$(PPh)_2[\mu\text{-}C(OCH_2CH_2CH_2CH_2OMe)H]$ (slower moving product). $Co_4(CO)_9(PPh)_2[\mu\text{-}C(OMe)H]$ exhibited the following spectral properties. IR (hexane): ν_{CO} 2066 (w), 2033 (vs), 2021 (s), 2008 (vs), 1996 (w), 1879 (m) cm^{-1}. $^{31}P\{^1H\}$ NMR (CDCl$_3$, -60 °C): δ 183.4 (1, d, $J_{\mu_4\text{-}P\text{-}\mu_4\text{-}P}$ = 227 Hz), 127.1 (1, d, $J_{\mu_4\text{-}P\text{-}\mu_4\text{-}P}$ = 227 Hz). $^{13}C\{^1H\}$ NMR (CD$_2$Cl$_2$, -90 °C): δ 239.0 (1, μ-carbonyl) 235.0 (1, μ-carbene, $J_{H\text{-}C}$ = 152 Hz), 204.0 (6, terminal carbonyls), 202.0 (2, terminal carbonyls). $^{13}C\{^1H\}$ NMR (C$_6$D$_6$, 25 °C): δ 59.2 (1, methoxy). ^1H NMR (CDCl$_3$, 25 °C): δ 11.12 (1, μ-CH, $J_{P\text{-}H}$ = 7.3 Hz), 4.02 (3, methoxy). Yield: 0.1 g (16.4%). $Co_4(CO)_9$-$(PPh)_2[\mu\text{-}C(OCH_2CH_2CH_2CH_2OMe)H]$ exhibited the following spectral properties. IR (hexane): ν_{CO} 2065 (w), 2033 (vs), 2019 (s), 2007 (vs), 1995 (w), 1877 (m) cm^{-1}. $^{31}P\{^1H\}$ NMR (CDCl$_3$, -60 °C): δ 182.2 (1, d, $J_{\mu_4\text{-}P\text{-}\mu_4\text{-}P}$ = 227 Hz), 152.2 (1, d, $J_{\mu_4P\text{-}\mu4P}$ = 227 Hz). $^{13}C\{^1H\}$NMR (C$_6$D$_6$, 25 °C): δ 81.4 (1, OCH$_2$), 72.1 (1, OCH$_2$), 58.4 (1, methoxy), 26.7 (1, CH$_2$), 26.5 (1, CH$_2$). ^1H NMR (CDCl$_3$, 25 °C): δ 11.26 (1, μ-CH, $J_{P\text{-}H}$ = 7.3 Hz), 4.24 (2, OCH$_2$), 3.46 (2, OCH$_2$), 3.33 (3, methoxy), 1.83 (4, methylene groups). Yield: 0.2 g (31.1%).

Reaction of $Co_4(CO)_9(PPh)_2CHO^-Li^+$ with Trifluoroacetic Anhydride. To 20 mL of THF containing 0.41 mmol of III at -78 °C was added 0.2 mL (1.42 mmol) of trifluoroacetic anhydride. The reaction was stirred with warming overnight. The reaction mixture was then concentrated to dryness in vacuo. The residue was extracted with hexane until the washings were colorless to afford $Co_4(CO)_9(PPh)_2[\mu\text{-}C(O_2CCF_3)H]$ as a red solid in ~60% yield. IR (hexane): ν_{CO} 2068 (w), 2045 (vs), 2031 (s), 2019 (vs), 1885 (m), 1787 (w, trifluoroacetyl C=O). $^{31}P\{^1H\}$ NMR (CDCl$_3$, 25 °C): δ 206.0 (1, b), 159.0 (1, b). ^1H NMR (CDCl$_3$, 25 °C): δ 11.2 (1, μ-C-H, $J_{P\text{-}H}$ = 7.8 Hz). Attempts to purify VI by column chromatography over silica gel led only to a quantitative recovery of the parent cluster I. We did not examine the fate of the carbene moiety in this interesting transformation.

Reaction of $Co_4(CO)_9(PPh)_2COCH_3^-Li^+$ with Methyl Triflate. To 20 mL of THF containing 1.37 mmol of VII at -78 °C was added 0.16 mL (1.46 mmol) of methyl triflate. The reaction was stirred at -78 °C for 2.0 h, and the solvent was removed in vacuo accompanied by slow warming. The residue was extracted with hexane until the washings were colorless and examined by TLC (hexane/benzene, 8:2 v/v). It revealed the presence of two products, which were isolated by column chromatography, recrystallized from hexane, and subsequently identified as Co_4-$(CO)_9(PPh)_2[\mu\text{-}C(OMe)Me]$ (faster moving product) and Co_4-$(CO)_9(PPh)_2[\mu\text{-}C(OCH_2CH_2CH_2OMe)Me]$ (slower moving product). $Co_4(CO)_9(PPh)_2[\mu\text{-}C(OMe)Me]$ exhibited the following spectral properties. IR (hexane): ν_{CO} 2062 (w), 2031 (vs), 2016 (s), 2005 (s), 1989 (m), 1966 (w), 1877 (m) cm^{-1}. $^{31}P\{^1H\}$ NMR (CDCl$_3$, -60 °C): δ 156.1 (1, d, $J_{\mu_4\text{-}P\text{-}\mu_4\text{-}P}$ = 222 Hz), 131.2 (1, d, $J_{\mu_4P\text{-}\mu_4P}$ = 222 Hz). $^{13}C\{^1H\}$ NMR (CDCl$_3$, 25 °C): δ 59.3 (1, methoxy), 50.0 (1, methyl). ^1H NMR (CDCl$_3$, 25 °C): δ 3.9 (3, methoxy), 3.2 (3, methyl). Yield: 0.35 g (33.6%). Anal. Calcd for C$_{24}$H$_{16}$Co$_4$O$_{10}$P$_2$: C, 37.81; H, 2.10. Found: C, 37.63; H, 2.16. $Co_4(CO)_9(PPh)_2[\mu\text{-}C(OCH_2CH_2CH_2CH_2OMe)Me]$ displayed the following spectral properties. IR (hexane): ν_{CO} 2062 (w), 2029 (vs), 2015 (s), 2004 (vs), 1989 (m), 1966 (w), 1875 (m) cm^{-1}. $^{31}P\{^1H\}$ NMR (CDCl$_3$, -60 °C): δ 154.0 (1, d, $J_{\mu_4\text{-}P\text{-}\mu_4\text{-}P}$ = 222 Hz), 131.0 (1, d, $J_{\mu_4\text{-}P\text{-}\mu_4\text{-}P}$ = 222 Hz). $^{13}C\{^1H\}$ NMR (CDCl$_3$, 25 °C): δ 72.3 (1, OCH$_2$), 71.9 (1, OCH$_2$), 58.4 (1, methoxy), 50.2 (1, methyl), 26.9 (1, CH$_2$), 26.6 (1, CH$_2$). ^1H NMR (CDCl$_3$, 25 °C): δ 3.7 (2, b, OCH$_2$), 3.3 (2, b, OCH$_2$), 3.3 (6, b, methoxy and methyl), 1.9 (2, CH$_2$), 1.8 (2, CH$_2$). Yield: 0.32 g (28.1%). Anal. Calcd for C$_{28}$H$_{24}$Co$_4$O$_{11}$P$_2$·1/2hexane: C, 41.39; H, 3.32. Found: C, 41.33; H, 3.30.

Reaction of $Co_4(Co)_9(PPh)_2COCH_3^-$ Li$^+$ with Trifluoroacetic Anhydride. To 100 mL of a THF solution containing 1.37 mmol of VII at -78 °C was added 0.4 mL (excess) of trifluoroacetic anhydride. The stirring was continued for 2.0 h at -78 °C and the mixture allowed to warm to room temperature overnight. Solvent removal in vacuo afforded a red residue that was extracted with hexane until the extracts were colorless. The crude material was chromatographed over silica by using hexane as the eluant

and it was recrystallized from hexane to yield 0.62 g (62.0%) of red $Co_4(CO)_9(PPh)_2(\mu\text{—}C=CH_2)$. IR (hexane): 2041 (vs), 2028 (s), 2016 (s), 1882 (m) cm^{-1}. $^{31}P\{^1H\}$ NMR (CDCl$_3$, 25 °C): δ 179.9 (b s). $^{13}C\{^1H\}$ NMR (CDCl$_3$, 25 °C): δ 126.9 (1, CH$_2$). ^1H NMR (CDCl$_3$, 25 °C): δ 6.11 (2, CH$_2$). Anal. Calcd for C$_{23}$H$_{12}$Co$_4$O$_9$P$_2$: C, 37.82; H, 1.64. Found: C, 37.74; H, 1.66.

Reaction of $Co_4(CO)_9(PPh)_2COBu^-Li^+$ with Trifluoroacetic Anhydride. To 1.10 mmol of $Co_4(CO)_9(PPh)_2COBu^-Li^+$ (prepared in situ from I and BuLi) in 70 mL of THF at -78 °C was added 0.4 mL (excess) of trifluoroacetic anhydride. The reaction was stirred at -78 °C for 6.0 h and then overnight as it was allowed to warm to room temperature. The solution was concentrated to dryness in vacuo and extracted with hexane until all washings were colorless. It was chromatographed over silica gel with hexane as the eluant. Analytically pure $Co_4(CO)_9$-$(PPh)_2[\mu\text{—}C=C(CH_2CH_2Me)H]$ was obtained by recrystallization from hexane. Yield: 0.52 g (61.2%). IR (hexane): ν_{CO} 2068 (m), 2037 (vs), 2029 (s), 2019 (vs), 2012 (vs), 1987 (m), 1880 (m) cm^{-1}. $^{31}P\{^1H\}$ NMR (CDCl$_3$, -60 °C): δ 236.7 (1, s), 134.0 (1, s, b). $^{13}C\{^1H\}$ NMR (CDCl$_3$, 25 °C): δ 140.2 (1, β-vinylidene C), 38.2 (1, CH$_2$), 24.2 (1, CH$_2$), 13.8 (1, methyl). ^1H NMR (CDCl$_3$, 25 °C): δ 6.1 (1, t, β-vinylidene C-H, J = 7.1 Hz), 2.4 (2, q, CH$_2$, J = 7.1 Hz), 1.3 (2, m, CH$_2$, J = 7.1 Hz), 0.8 (3, q, methyl, J = 7.1 Hz). Anal. Calcd for C$_{26}$H$_{18}$Co$_4$O$_9$P$_2$: C, 40.43; H, 2.33. Found: C, 40.52; H, 2.38.

X-ray Diffraction Study of $Co_4(CO)_9(PPh)_2[\mu\text{-}C(OMe)Me]$. Single crystals suitable for diffraction analysis were grown in hexane at -40 °C, from which a very small burgundy plate, approximate dimensions 0.20 × 0.20 × 0.08 mm, was mounted on an Enraf-Nonius CAD-4 automatic diffractometer. The radiation used was Mo Kα monochromatized by a dense graphite crystal assumed for all purposes to be 50% imperfect. Final cell constants, as well as other information pertinent to data collection and refinement, are listed in Table I. The laue symmetry was determined to be 2/m, and the space group was shown unambiguously to be $P2_1/c$. The diffraction symmetry showed a strong tendency toward body centering, with the class of reflections having *h*, +*k*, +*l* odd being systematically weak but definitely observable. Intensities were measured by using the θ-2θ scan technique, with the scan rate depending on the net count obtained in rapid prescans of each reflection. Two standard reflections were monitored periodically during the course of the data collection as a check of crystal stability and electronic reliability. These showed no significant variation. In reducing the data, Lorentz and polarization factors were applied, as well as an empirical absorption correction based on azimuthal psi scans of five reflections having χ near 90°.[52] The structure was solved by MULTAN,[53] which showed all eight Co atoms in the two independent molecules that comprise the asymmetric unit. The remaining non-hydrogen atoms were found in subsequent difference Fourier syntheses. Since there were so many variables and so few observed data due to the very small size of the sample crystal, only the Co and P thermal parameters were refined anisotropically. Also, no attempt was made to locate the hydrogen atoms in difference maps or to position them ideally. After all shift/esd ratios were less than 0.4, the full-matrix least squares converged at the agreement factors listed in Table I. Anomalous dispersion coefficients for the heavier elements were included. No unusually high correlations were noted between any of the variables in the last cycle of least-squares refinement, and the final difference density map showed no peaks of electron density greater than 0.5 e Å^{-3}. All calculations were made by using Molecular Structure Corp.'s TEXRAY 230 modifications of the SDP-PLUS series of programs.

The two independent molecules of $Co_4(CO)_9(PPh)_2[\mu\text{-}C$-$(OMe)Me]$ (VII) represent the first examples of a heterosubstituted carbene cluster in this growing family of Co$_4$P$_2$-based clusters. Both molecules of VII are essentially identical within experimental error, except for slight differences in (a) the twist angle between the phosphinidene phenyl groups and (b) the Co-μ_4-P-C(aryl) bond angles. The observed phenyl twist angles

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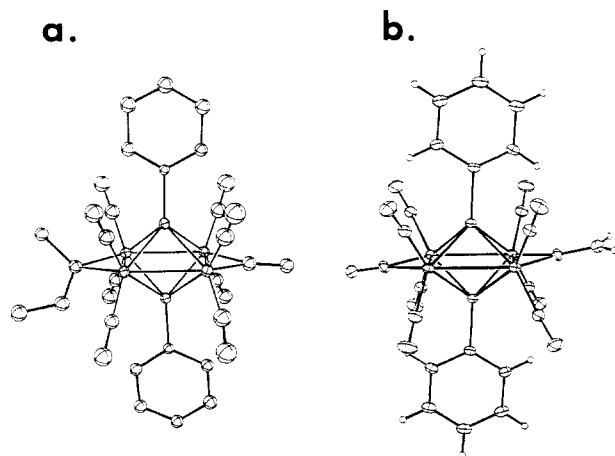
a.   **b.**

Figure 3. ORTEP diagram of (a) the carbene complex Co$_4$-(CO)$_9$(PPh)$_2$[μ-C(OMe)Me] (VIII) and (b) the vinylidene complex Co$_4$(CO)$_9$(PPh)$_2$(μ-C=CH$_2$) (X). For clarity, the hydrogen atoms in the former cluster have been omitted.

are 4.8° (see Figure 3a) and 13.2° (isomer not shown), while the Co–μ_4-P–C(aryl) bond angles are approximately 125°. The carbene-bridged and carbonyl-bridged Co–Co bond distances are similar with a mean length of 2.505 Å. They are 0.20 Å shorter than the nonbridged Co–Co lengths of 2.705 Å (average). The terminal Co–CO distances range from 1.650 (20) to 1.760 (20) Å with a mean distance of 1.713 Å. The Co–μ-C mean distances associated with the carbene and carbonyl moieties are 2.030 and 1.900 Å, respectively. The symmetrical capping nature of the μ_4-phenylphosphinidene moiety is manifested by the similar Co–μ_4-P lengths of 2.237 Å (average). These compare well with those in the parent cluster Co$_4$(CO)$_{10}$(PPh)$_2$.[6b,54] The presence of the methoxymethylcarbene moiety exerts no unusual destabilizing perturbation upon the cluster core as judged by bond lengths and angles that are in good agreement with those in Co$_4$(CO)$_{10}$(PPh)$_2$ and other Co$_4$–phosphinidene capped clusters.[6b,9,54]

X-ray Diffraction Study of Co$_4$(CO)$_9$(PPh)$_2$(μ-C=CH$_2$). Single crystals suitable for diffraction analysis were grown by evaporating a hexane solution of Co$_4$(CO)$_9$(PPh)$_2$(μ—C=CH$_2$). From these crystals a large dark burgundy prismatic block of dimensions 0.60 × 0.30 × 0.20 mm was mounted on a glass fiber in a random orientation on an Enraf-Nonius CAD-4 automatic diffractometer. The Laue symmetry was determined to be 2/m, and from the systematic absences noted the space group was shown unambiguously to be $P2_1/n$. Intensities were measured by using the θ–2θ scan technique, with the scan rate depending on the net count obtained in rapid prescans of each reflection. Two standard reflections were monitored periodically during the course of the data collection as a check of crystal stability and electronic reliability, and these did not vary significantly. In reducing the data, Lorentz and polarization factors were applied, as well as an empirical absorption correction based on azimuthal psi scans of six reflections having χ near 90°.[52] Since there are only two molecules in the unit cell, it was immediately apparent that the crystal structure was disordered with respect to the bridging carbonyl and vinyl groups. The structure was solved by MULTAN,[53] which revealed the positions of the two Co and one P atoms in the asymmetric unit, which comprised only one-half molecule situated about an inversion center. The remaining non-hydrogen atoms were found in subsequent difference Fourier synthesis. The usual sequence of isotropic and anisotropic refinement was followed, after which all hydrogens were entered in ideally calculated positions. The problem of the disordered bridging groups was solved by placing O(1) and C(1A) at theoretical positions having populations of 0.5, and with fixed isotropic thermal parameters. Full-matrix refinement proved unsuccessful due to the high correlations found between two atoms having refineable positions in such close proximity. Therefore the method of block-diagonal least squares had to be used, with each individual

atom comprising a separate block. After all shift/esd ratios were less than 0.5, convergence was reached at the agreement factors listed in Table I. At this point, the C(1)–O(1) and C(1)–C(1A) bond lengths were within acceptable ranges noted in previous structural determinations, and thus it can be concluded that the molecule does indeed consist of one bridging carbonyl and one bridging vinyl group. The final difference density map showed no peaks greater than 0.20 e Å^{-3}. The final fractional coordinates are included in Table IV.

Co$_4$(CO)$_9$(PPh)$_2$(μ-C=CH$_2$) is the first structurally characterized vinylidene derivative of the Co$_4$–phosphinidene capped cluster. Although the μ-bridging carbonyl and vinylidene groups were disordered in the unit cell, the spectroscopic properties (^{1}H, ^{13}C, and ^{31}P NMR) unequivocally recorded the presence of the β-vinylidene carbon (vide supra) and established the validity of the X-ray crystallographic results. The structural data for X closely parallel that observed in Co$_4$(CO)$_{10}$(PPh)$_2$. For example, the non-carbonyl-bridged Co–Co bond distance is 2.717 (a) Å, while the shorter, bridged Co–Co bond distance is 2.504 (1) Å. These are 0.02 Å longer and 0.02 Å shorter than the corresponding distances in Co$_4$(CO)$_{10}$(PPh)$_2$.[6b,54] The terminal Co–CO bond distances range from 1.800 (2) to 1.805 (2) Å with a mean average length of 1.801 Å. The Co–μ_4-P distances display a mean distance of 2.242 Å as expected for a symmetrically bound μ_4-phosphinidene moiety. Finally, the tetracobalt cluster experiences no extenuating perturbations as a result of the μ-vinylidene substituent.

Decomposition Studies of the Formyl Cluster Co$_4$(CO)$_9$-(PPh)$_2$CHO$^-$Li$^+$. The decomposition of the formyl cluster III was examined with and without added tri-n-butyltin hydride (Bu$_3$SnH). The experiment and procedure are described in detail first for the formyl decomposition in the absence of added Bu$_3$SnH. To 0.1 g (0.14 mmol) of Co$_4$(CO)$_{10}$(PPh)$_2$ in 10 mL of THF at –78 °C was added 0.15 mL of a 1.0 M solution of LiEt$_3$BH in THF. The solution turned brown immediately to signal the formation of the formyl cluster. An aliquot of the solution was rapidly withdrawn and placed in a nitrogen purged IR cell (25 °C) equipped with septum caps. The progress of decomposition was monitored by observing the change in the metal carbonyl region (2200–1500 cm^{-1}) as a function of time. After 40 min, no formyl cluster was observed. Instead the hydride cluster Co$_4$-(CO)$_9$(PPh)$_2$(μ-H) was present as the major organometallic constituent as determined by its IR bands at 1985 and 1833 cm^{-1}. The reaction in the presence of Bu$_3$SnH (0.68 mmol) was performed similarly. The IR spectral changes with added Bu$_3$SNH were essentially identical with the previously described decomposition experiment. From the absence of an inhibitory effect of n-BuSNH on the formyl decomposition, we concluded that the radical chain decomposition of III was unimportant.

Reaction of Co$_4$(CO)$_9$(PPh)$_2$CHO$^-$Li$^+$ with Trifluoroacetic Acid. To 0.15 g (0.21 mmol) of Co$_4$(CO)$_{10}$(PPh)$_2$ in 8.0 mL of THF at –78 °C was added 0.25 mL of a 1.0 M solution of LiEt$_3$BH in THF. The reaction to afford the formyl cluster was immediate as observed by the discharge of the red color of Co$_4$(CO)$_{10}$(PPh)$_2$, followed by the appearance of the brown formyl solution. To the formyl cluster was added 0.25 mL (excess) of trifluoroacetic acid at –78 °C. The IR spectrum of the solution was then quickly examined as the temperature rose from –78 to +25 °C. It revealed a consistent shift of all the carbonyl stretching bands to higher energies. The solution was then allowed to warm slowly to room temperature overnight with stirring. The IR spectrum showed the parent cluster I to be present as the sole organometallic species. After solvent removal, the residue was extracted with hexane. Chromatographic workup on silica gel with hexane as eluant indicated the presence of I in essential quantitative yield (~90%) as judged by the IR and ^{31}P NMR spectra in comparison with that of authentic I.

Reaction of Co$_4$(CO)$_9$(PPh)$_2$CHO$^-$Li$^+$ with Iron Pentacarbonyl. To 0.11 g (0.15 mmol) to Co$_4$(CO)$_{10}$(PPh)$_2$ in 13 mL of THF at –60 °C was added 0.16 mL of 1.0 M LiEt$_3$BH in THF. The reaction was stirred at –60 °C for 2.0 h, after which 0.02 mL (0.15 mmol) of Fe(CO)$_5$ was added. The mixture was stirred overnight with warming to room temperature. Examination of the solution showed carbonyl bands characteristic of the parent cluster (yield ~85%). In addition, a carbonyl band at 1559 cm^{-1} was assigned to that of Fe(CO)$_4$CHO$^-$Li$^+$.[28] The solvent was removed in vacuo to afford a red residue. It was examined by

(54) Ryan, R. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6904.

Table IV. Final Positional Parameters for the Non-hydrogen Atoms of the Carbene Derivatives of VIII and X

$Co_4(CO)_9(PPh)_2[\mu\text{-}C(OMe)Me]$ (VIII)

atom	x	y	z	B, Å²	atom	x	y	z	B, Å²
Co(1')	0.2454 (2)	0.6267 (1)	0.9001 (2)	3.14 (8)	Co(1)	0.1447 (2)	0.1277 (1)	0.8885 (2)	3.18 (9)
Co(2')	0.3736 (2)	0.6223 (1)	1.0503 (2)	3.72 (9)	Co(2)	0.2468 (2)	0.1939 (1)	1.0026 (2)	3.26 (9)
Co(3')	0.2601 (2)	0.6074 (1)	1.1365 (2)	3.92 (9)	Co(3)	0.3281 (2)	0.1087 (1)	1.1120 (2)	3.41 (9)
Co(4')	0.1326 (2)	0.6135 (1)	0.9843 (2)	3.51 (9)	Co(4)	0.2270 (2)	0.0407 (1)	1.0003 (2)	3.15 (9)
P(1')	0.2574 (4)	0.5657 (3)	1.0096 (4)	3.7 (2)	P(1)	0.2895 (4)	0.1133 (3)	0.9589 (4)	3.3 (2)
P(2')	0.2509 (4)	0.6691 (3)	1.0274 (4)	3.2 (2)	P(2)	0.1814 (4)	0.1211 (3)	1.0397 (3)	3.0 (2)
O(1')	0.086 (1)	0.5964 (7)	1.143 (1)	7.1 (5)*	O(1)	0.3506 (9)	−0.0064 (6)	1.1724 (9)	4.9 (4)*
O(2')	0.202 (1)	0.5427 (7)	0.758 (1)	6.9 (5)*	O(2)	0.142 (1)	0.1036 (7)	0.709 (1)	7.3 (5)*
O(3')	0.165 (1)	0.7255 (7)	0.790 (1)	6.1 (5)*	O(3)	−0.038 (1)	0.1088 (7)	0.843 (1)	7.0 (5)*
O(4')	0.505 (1)	0.5357 (7)	1.119 (1)	7.8 (5)*	O(4)	0.386 (1)	0.2550 (7)	0.975 (1)	6.7 (5)*
O(5')	0.481 (1)	0.7127 (7)	1.152 (1)	6.8 (5)*	O(5)	0.208 (1)	0.2679 (7)	1.126 (1)	7.05 (5)*
O(6')	0.331 (1)	0.5085 (9)	1.246 (1)	10.3 (6)*	O(6)	0.512 (1)	0.1251 (8)	1.151 (1)	8.9 (5)*
O(7')	0.305 (1)	0.6825 (7)	1.290 (1)	7.3 (5)*	O(7)	0.328 (1)	0.1509 (8)	1.281 (1)	8.7 (5)*
O(8')	0.018 (1)	0.5242 (8)	0.878 (1)	8.3 (5)*	O(8)	0.272 (1)	−0.0402 (8)	0.891 (1)	8.7 (6)*
O(9')	0.008 (1)	0.7030 (7)	0.918 (1)	6.7 (5)*	O(9)	0.087 (1)	−0.0264 (7)	1.019 (1)	6.6 (5)*
O(10')	0.3968 (9)	0.6894 (7)	0.9105 (9)	5.5 (4)*	O(10)	0.0751 (9)	0.2331 (6)	0.9049 (9)	5.4 (4)*
C(1')	0.138 (2)	0.602 (1)	1.107 (1)	5.9 (7)*	C(1)	0.316 (1)	0.031 (1)	1.119 (1)	4.9 (6)*
C(2')	0.220 (1)	0.576 (1)	0.816 (1)	5.1 (7)*	C(2)	0.143 (1)	0.113 (1)	0.784 (1)	6.0 (7)*
C(3')	0.200 (1)	0.685 (1)	0.835 (1)	5.6 (7)*	C(3)	0.039 (1)	0.119 (1)	0.864 (1)	5.4 (6)*
C(4')	0.452 (2)	0.573 (1)	1.090 (2)	6.7 (8)*	C(4)	0.329 (1)	0.230 (1)	0.984 (1)	5.3 (7)*
C(5')	0.440 (1)	0.677 (1)	1.108 (1)	5.7 (7)*	C(5)	0.223 (1)	0.2376 (9)	1.076 (1)	4.6 (6)*
C(6')	0.301 (2)	0.548 (1)	1.198 (2)	8.9 (9)*	C(6)	0.441 (1)	0.117 (1)	1.137 (1)	6.7 (7)*
C(7')	0.286 (2)	0.653 (1)	1.228 (1)	6.2 (7)*	C(7)	0.328 (2)	0.127 (1)	1.214 (1)	6.8 (7)*
C(8')	0.065 (2)	0.559 (1)	0.924 (2)	6.6 (8)*	C(8)	0.257 (2)	−0.007 (1)	0.938 (2)	6.5 (7)*
C(9')	0.057 (1)	0.667 (1)	0.949 (1)	5.6 (7)*	C(9)	0.141 (1)	0.001 (1)	1.012 (1)	5.7 (7)*
C(10')	0.374 (1)	0.6345 (9)	0.925 (1)	4.3 (6)*	C(10)	0.143 (1)	0.2135 (9)	0.884 (1)	4.1 (6)*
C(11')	0.419 (1)	0.5912 (9)	0.884 (1)	4.6 (6)*	C(11)	0.160 (1)	0.2435 (9)	0.807 (1)	4.3 (6)*
C(12')	0.437 (2)	0.705 (1)	0.847 (2)	6.4 (7)*	C(12)	0.025 (2)	0.282 (1)	0.861 (2)	6.7 (8)*
C(13')	0.257 (1)	0.4881 (9)	1.001 (1)	3.9 (6)*	C(13)	0.366 (1)	0.1061 (9)	0.903 (1)	2.5 (5)*
C(14')	0.317 (1)	0.464 (1)	0.966 (1)	4.7 (6)*	C(14)	0.357 (1)	0.140 (1)	0.831 (1)	5.0 (7)*
C(15')	0.317 (2)	0.402 (1)	0.966 (2)	6.4 (7)*	C(15)	0.418 (1)	0.134 (1)	0.786 (1)	5.9 (7)*
C(16')	0.255 (2)	0.375 (1)	0.992 (2)	7.6 (7)*	C(16)	0.486 (2)	0.097 (1)	0.823 (1)	6.0 (7)*
C(17')	0.190 (2)	0.400 (1)	1.023 (2)	7.3 (8)*	C(17)	0.495 (1)	0.063 (1)	0.896 (1)	5.4 (7)*
C(18')	0.198 (2)	0.461 (1)	1.031 (2)	6.0 (7)*	C(18)	0.435 (1)	0.0700 (9)	0.938 (1)	3.9 (6)*
C(19')	0.251 (1)	0.7460 (9)	1.043 (1)	3.1 (6)*	C(19)	0.105 (1)	0.1229 (9)	1.097 (1)	2.9 (5)*
C(20')	0.297 (1)	0.7774 (9)	1.002 (1)	4.0 (6)*	C(20)	0.034 (1)	0.1592 (9)	1.070 (1)	4.0 (6)*
C(21')	0.302 (1)	0.897 (1)	1.020 (1)	5.6 (7)*	C(21)	−0.027 (1)	0.156 (1)	1.114 (1)	4.5 (6)*
C(22')	0.259 (1)	0.8590 (9)	1.073 (1)	4.4 (6)*	C(22)	−0.013 (1)	0.117 (1)	1.185 (1)	4.3 (6)*
C(23')	0.208 (1)	0.8268 (9)	1.108 (1)	4.1 (6)*	C(23)	0.059 (1)	0.082 (1)	1.214 (1)	4.9 (7)*
C(24')	0.203 (1)	0.7667 (9)	1.094 (1)	2.9 (5)*	C(24)	0.122 (1)	0.0852 (9)	1.173 (1)	3.9 (6)*

$Co_4(CO)_9(PPh)_2(\mu\text{-}C{=}CH_2)$ (X)

atom	x	y	z	B, Å²	atom	x	y	z	B, Å²
Co(1)	0.91376 (4)	0.39165 (3)	0.57238 (4)	2.731 (9)	C(3)	0.8310 (4)	0.2834 (3)	0.4831 (4)	3.65 (8)
Co(2)	1.13758 (4)	0.41835 (3)	0.45443 (4)	2.760 (9)	C(4)	1.2714 (4)	0.3572 (3)	0.5670 (4)	3.64 (8)
P	0.92972 (9)	0.48252 (6)	0.38793 (8)	2.71 (2)	C(5)	1.1375 (4)	0.3359 (3)	0.3129 (4)	3.74 (8)
O(1)	0.6548 (5)	0.4582 (4)	0.6544 (5)	4.00	C(6)	0.8196 (3)	0.4554 (2)	0.2336 (3)	2.77 (6)
O(2)	0.9836 (3)	0.2824 (2)	0.8229 (3)	5.54 (7)	C(7)	0.6853 (4)	0.4314 (3)	0.2365 (9)	3.35 (7)
O(3)	0.7869 (3)	0.2107 (2)	0.4311 (3)	5.78 (7)	C(8)	0.5994 (4)	0.4104 (3)	0.1198 (4)	3.94 (8)
O(4)	1.3525 (3)	0.3165 (2)	0.6361 (3)	5.67 (7)	C(9)	0.6482 (4)	0.4139 (3)	0.0021 (4)	4.22 (8)
O(5)	1.1434 (3)	0.2856 (2)	0.2245 (3)	6.35 (8)	C(10)	0.7810 (4)	0.4379 (3)	−0.0008 (4)	4.40 (9)
C(1)	0.7582 (3)	0.4703 (3)	0.6065 (3)	3.25 (7)	C(11)	0.8689 (4)	0.4589 (3)	0.1151 (3)	3.77 (8)
C(2)	0.9594 (3)	0.3276 (3)	0.7290 (3)	3.50 (8)	C(1A)	0.6297 (8)	0.4582 (6)	0.6323 (7)	4.00

a Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$. Asterisk identifies atom refined isotropically.

^{1}H NMR spectroscopy after the addition of a THF solution containing 0.3 M $LiCLO_4$ (as an external ^{7}Li lock) and o-dimethoxybenzene (0.05 mmol as an internal standard). ^{1}H NMR analysis revealed the presence of a low-field formyl resonance of δ 14.26 (~60% by integration). No μ-bridging hydride cluster $Co_4(CO)_9(PPh)_2(\mu\text{-}H)^-$ was observed. In analogous reactions, the parent cluster was isolated by chromatography over silica gel using hexane as the eluant (yield ~80%) after ^{1}H NMR spectral quantitation of $Fe(CO)_4(CHO)^-Li^+$. The deuteriated formyl cluster $Co_4(CO)_9(PPh)_2CDO^-Li^+$. The deuteriated formyl cluster $Co_4(CO)_9(PPh)_2CDO^-Li^+$ was prepared from $LiEt_3BD$ (Aldrich) under analogous conditions. Treatment of the deuterioformyl cluster III-d_1 with a stoichiometric amount of $Fe(CO)_5$ led to only $Fe(CO)_4CDO^-Li^+$. The latter was identified from its ^{2}H NMR spectrum (δ 14.17) in 70% yield. The parent cluster I was isolated in near quantitative yield (~90%) after column chromatography.

Reaction of $Co_4(CO)_9(PPh)_2[\mu\text{-}C(OMe)Me]$ with Fluoroboric Acid. To 0.057 g (0.075 mmol) of $Co_4(CO)_9(PPh)_2[\mu\text{-}C\text{-}(OMe)Me]$ in 6 mL of toluene at −78 °C was added 0.03 mL of

$HBF_4\cdot Et_2O$ in Et_2O (54% v/v). IR analysis after 2.0 h at −78 °C revealed that no reaction had occurred. Only the spectrum of the cluster VIII was observed. The solution was gradually warmed to room temperature and stirred overnight. TLC analysis (hexane/benzene, 8:2 v/v) showed the presence of the vinylidene cluster $Co_4(CO)_9(PPh)_2(\mu\text{—}C{=}CH_2)$ and much material at the origin. The starting methoxymethylcarbene cluster was not observed by TLC analysis. The ^{31}P and ^{1}H NMR spectra of the residue showed resonances at δ 181 and 6.11, respectively, which were assigned to the vinylidene cluster X. The remaining components of the reaction mixture were not identified.

III-*d*, 106733-94-2; IV, 106733-95-3; V, 106733-96-4; VI, 106733-97-5; VII, 106733-93-1; VIII, 106733-98-6; IX, 106733-99-7; X, 106734-00-3; XI, 106734-01-4; Fe(CO)₄CHO⁻, 48055-09-0; Fe(CO)₅, 13463-40-6; Co, 7440-48-4.

Hydrosilylation with Platinum Complexes. Preparation, Low-Temperature NMR Spectra, and X-ray Crystal Structure of the Novel Bis-Olefin Catalyst *cis*-PtCl₂(PhCH=CH₂)₂

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The bis-olefin complex *cis*-PtCl₂(PhCH=CH₂)₂ (1) has been prepared and shown to exist in several isomeric forms by ¹H and ¹⁹⁵Pt NMR spectroscopy. Complex 1 is a synthetically useful form of soluble PtCl₂ and also catalyzes the hydrosilylation of styrene with Et₃SiH. This latter reaction has been carried out with a variety of known complexes of platinum(II), and the results have been compared with those found for some trichlorostannate complexes of platinum. One isomer of 1 has been crystallized and its structure determined by X-ray diffraction. Crystal data for this isomer: space group $P2_1/c$, a = 13.805 (7) Å, b = 10.235 (2) Å, c = 10.985 (7) Å, β = 106.51 (4)°; Z = 4; V = 1489.1 Å³.
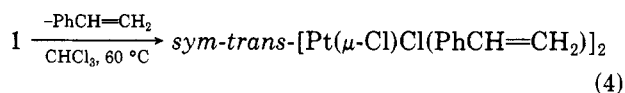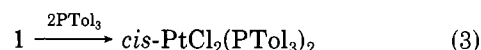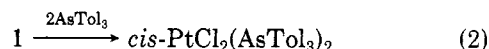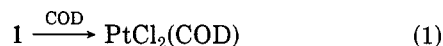
Introduction

The hydrosilylation of olefins, followed by further transformations of the alkylsilanes that form, provides a useful route to a variety of organic substrates.[1] In the realm of platinum chemistry the most commonly utilized catalyst precursor is H₂PtCl₆,[1,2] although this Pt(IV) complex is certainly reduced to Pt(II) during the reaction.[2] Our previous studies on trichlorostannate complexes of Pt(II) revealed these to be more labile than the corresponding chloro complexes,[3,4] so that we considered it useful to compare several of our trichlorostannate compounds with known hydrosilylation catalysts. We report here the results of these tests as well as the preparation, molecular structure, and extensive NMR spectroscopic studies of *cis*-PtCl₂(PhCH=CH₂)₂, a possible intermediate in the hydrosilylation of styrene with triethylsilane and the first characterized bis monodentate olefin complex of Pt(II).

Results and Discussion

***cis*-PtCl₂(PhCH=CH₂)₂ Chemistry.** During our hydrosilylation catalysis we observed that styrene, PhCH=CH₂, readily dissolved PtCl₂. In view of the normal sparing solubility of PtCl₂ in noncoordinating solvents we assumed that a styrene complex was formed and have isolated this material that precipitates slowly from styrene. The compound so obtained was *cis*-PtCl₂(PhCH=CH₂)₂ (1) that

is readily distinguishable from the dimer *sym-trans*-[Pt-(μ-Cl)Cl(PhCH=CH₂)]₂ by ¹H and ¹⁹⁵Pt NMR as well as by IR and microanalytical data. Moreover, the analogous para Cl styrene analogue is also synthetically accessible (see Experimental Section).

Complex 1 reacts in a predictable fashion with a variety of reagents, e.g., 1,5-cyclooctadiene (COD), 2 equiv of AsTol₃ (Tol = (C₆H₄-*p*-CH₃ or 2 equiv of PTol₃ (or PPh₃), or by dissociation of 1 equiv of PhCH=CH₂ to give the known complexes shown in eq 1–4, and consequently 1 can serve as a source of "soluble" PtCl₂ for synthetic purposes.

$$1 \xrightarrow{\text{COD}} \text{PtCl}_2(\text{COD}) \tag{1}$$

$$1 \xrightarrow{\text{2AsTol}_3} \textit{cis-}\text{PtCl}_2(\text{AsTol}_3)_2 \tag{2}$$

$$1 \xrightarrow{\text{2PTol}_3} \textit{cis-}\text{PtCl}_2(\text{PTol}_3)_2 \tag{3}$$

$$1 \xrightarrow[\text{CHCl}_3,\ 60\ °\text{C}]{\text{-PhCH=CH}_2} \textit{sym-trans-}[\text{Pt}(\mu\text{-Cl})\text{Cl}(\text{PhCH=CH}_2)]_2 \tag{4}$$

In solution 1 reveals several isomers whose identification is made easier by the following NMR observations.

(1) The compounds have similar ¹⁹⁵Pt and ¹³C chemical shifts[6] (see Tables I and II), and this is consistent with isomers and not ligand dissociation or cis–trans isomerization.

(2) The ¹H vinyl proton chemical shifts are determined, in part, by the proximity of a styrene phenyl group to a vinyl proton on a *second* coordinated styrene.

Point 2 is important, but not obvious. Consider **1a**; the molecular structure of this isomer (discussed in the next section) clearly shows that both olefins are roughly per-

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