Table I. Selected Bond Distances (Å) and Angles (deg) for 3

(a) Bond Distances

Rh-P	2.279 (1)	P-(H1P)	1.40 (3)	Si(3)-C(3)	1.920 (3)
Si(2)-C(3)	1.886 (3)	Rh-C(1)	2.159 (2)	C(1)-H(1)	0.88 (3)
Si(3)-C(1)	1.849 (3)	P-C(3)	1.827 (2)	P···C(1)	2.778 (3)
Si(3)-C(12)	1.881 (2)				

(b) Bond Angles

Rh-P-C(3)	107.1 (1)	P-C(3)-Si(2)	115.2 (1)	Rh-P-C(2)	107.5 (1)
C(1)-Si(3)-C(3)	104.9 (1)	Rh-C(1)-Si(3)	102.8 (1)	C(2)-P-C(3)	103.9 (1)
C(3)-Si(3)-C(12)	106.9 (1)	C(14)-Rh-C(17)	81.7 (1)	C(1)-Si(3)-C(12)	116.3 (1)
C(3)-Si(3)-C(13)	112.9 (1)	C(17)-Rh-C(18)	36.4 (1)		

distances and angles are presented in Table I.

The unusual bidentate, heterocyclic ligand can be viewed as a *cis*-bicyclo[2.2.1]heptane (norbornane) analogue that has a rhodium atom at the bridgehead position.

Formation of 3 involves the activation of Rh-C, C-Si, and C-H bonds as well as the elimination of CH_4 and isobutene. The drive to form the new Rh-P and Rh-C bonds is assisted by the increased entropy of the products and the ease at which the volatile products can be removed. The production of 3 results in a buildup of ring strain. Considerable distortion occurs at C(1), C(2), and C(3) where the Si(1)-C(1)-Si(3), Si(1)-C(2)-Si(4), and Si(3)-C(3)-Si(2) angles are 117.6 (1)°, 121.2 (1)°, and 120.6 (1)°. The Rh-C(1)-Si(1), P-C(2)-Si(1), and P-C(3)-Si(3) angles are 100.3 (1)°, 101.5 (1)°, and 101.7 (1)°. These angles differ widely from those of a tetrahedral carbon (109.5°). The Si(1)-C(2) and Si(3)-C(3) bond distances are very long (~1.92 Å), which provides further evidence for ring strain. The rhodium atom is in a distorted square-planar geometry with the P-Rh-C(1) angle being 77.5(1)°. The compression of this angle from the normal square-planar angle of 90° is related to the length of the Si(1)-C(2) and Si(3)-C(3) bonds. Wider angles would require additional stretching of these bonds, and they are already lengthened considerably (1.92 Å) from that of a typical Si-C bond (1.85 Å).

The cyclooctadiene group exists in the expected boat configuration with the C(14)-C(21) and C(17)-C(18) bond distances of 1.381 (4) Å and 1.378 (5) Å, respectively. The four olefinic carbon to rhodium bond distances range from 2.157 (2) to 2.217 (3) Å.

The X-ray structure of 3 agrees with the spectroscopic data obtained:[19] ^{1}H NMR (200 MHz, C_6D_6, ppm) 5.00, 4.26 (br s, 4 H, COD vinyl protons), 4.12 (d of d, 1 H, $^1J_{P-H}$ = 292.3 Hz, $^3J_{PH-CH}$ = 5.5 Hz, P-H), 2.18, 1.98 (br m, 8 H, exo and endo methylene protons of COD), 0.49, 0.40 (s, 12 H, SiMe_2), 0.30 (s, 18 H, SiMe_3); $^{31}P\{^1H\}$ NMR (81 MHz, C_6D_6, ppm) -15.2 (d, $^1J_{Rh-P}$ = 152.3 Hz).

The reaction of di-*tert*-butyl phosphine with 1 at 25 °C in benzene-d_6 produces a number of products. We have monitored the reaction by ^{31}P NMR and witnessed the immediate disappearance of the free phosphine peak at +20 ppm with the subsequent production of many peaks downfield. A number of these peaks can be assigned to phosphine-bound rhodium species as they exhibit $^1J_{Rh-P}$ of between 110 and 190 Hz and have large $^1J_{P-H}$ (~300 Hz). We have obtained colorless crystals from cooling hexane solutions and will present their structures in a full account of this work.[21]

Acknowledgment.

Supplementary Material Available: Tables of bond distances and angles, structure factors, and positional and thermal parameters (38 pages). Ordering information is given on any current masthead page.

Synthesis of Trinuclear Alkylidyne Complexes from Dinuclear Alkyne Complexes and Metal Hydrides. CIDNP Evidence for Vinyl Radical Intermediates in the Hydrogenolysis of These Clusters

Paul F. Seidler, Henry E. Bryndza, Jane E. Frommer, Louis S. Stuhl, and Robert G. Bergman*
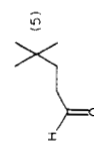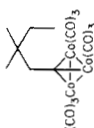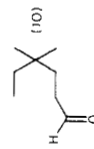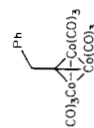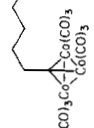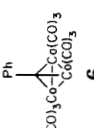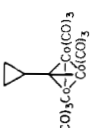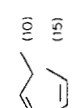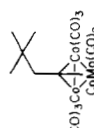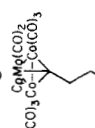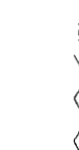
Department of Chemistry, University of California Berkeley, California 94720

Summary: Treatment of dicobalt alkyne complexes $Co_2(CO)_6(HCCR)$ (R = alkyl, aryl) with H_2 and $Co_2(CO)_8$ or $CpMo(CO)_3H$ leads to μ_3-alkylidyne complexes with molecular formula $Co_3(CO)_9CCH_2R$ and $CpMo(CO)_2Co_2-(CO)_6CCH_2R$, respectively, in high yield and purity. Hydrogenation of these clusters occurs under mild conditions (60-90 °C, benzene solution, 3-4 atm of H_2) and gives olefins, paraffins, and carbonyl compounds. A radical pathway for the hydrogenolyses is suggested by the observation of CIDNP in the olefinic product from some of the trinuclear clusters. Isotope labeling studies on the reaction of $Co_3(CO)_9CCH_2C(CH_3)_3$ (2) with H_2 are consistent with the intervention of vinyl radical intermediates.

Although metal-carbon bond hydrogenolysis is an important step in many catalytic processes, relatively few direct mechanistic investigations of this reaction exist.[1] We have undertaken a study of homogeneous reactions of trinuclear alkylidyne complexes with hydrogen to inves-

(18) X-ray diffraction data for RhC_21H_44PSi_4, 3: crystal system, triclinic; space group P$\bar{1}$, No. 2; cell dimensions at 140 K; a = 10.554 (2) Å, b = 11.239 (2) Å, c = 13.189 (2) Å; α = 103.00 (1)°, β = 101.27 (1)°, γ = 108.09 (2)°; V = 1388.3 (5) Å³; Z = 2; μ(Mo Kα) = 8.38 cm^{-1}; crystal size = 0.22 × 0.27 × 0.37 mm; yellow prisms; ρ^{298K}(exptl) = 1.279 g·cm^{-3}, ρ^{140K}(calcd) = 1.30 g·cm^{-3}; diffractometer, Syntex P2₁; radiation, graphite-monochromated Mo Kα; data collection temperature, 140 K; scan range, 1°; scan speed, 15° min^{-1}; 2θ range 0-55°; reflections collected, 6349 unique, 5807 with F_o > 3σ(F$_o$). All calculations were carried out on a Data General ECLIPSE computer using the SHELXTL program system. The atomic form factors including anomalous scattering were from ref 14. The data was corrected for absorption. The structure was solved by a combination of Patterson and difference Fourier techniques. All of the hydrogen atoms were located and refined: R = 0.031 with non-hydrogen atoms assigned anisotropic and hydrogen atoms assigned isotropic thermal parameters; R_w = 0.027, weighting scheme 1/σ^2(F).

(19) ^{1}H and ^{31}P NMR data were obtained on a NT-200 spectrometer operating at 200 and 81 MHz. All samples were run in freshly dried and distilled benzene-d_6. 85% H_3PO_4 was used as an external standard for the ^{31}P spectra.

(20) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, 1962; Vol. 3.

(21) One of the crystalline products of obtained is Rh(η^4-1,5-COD)(η^3-2-Me-C_3H_6)[HP(*t*-C_4H)_2].

Table I. Synthesis and Hydrogenolysis of Dinuclear Alkylidyne Complexes

compound	yield, %	color	hydrogenation products (yields)[a] olefin	alkane	carbonyl compd	hydrogenation temp, °C	product showing CIDNP
2	80	red-purple	(75)	(20)	(5)	60	(structure)
3	36	red-purple	(75)	(15)	(10)	60	(structure)
4	85	red-purple	Ph (25)	Ph (75)		85	none
5	68	red-purple	(40) (10) (10)	(40)	(4)	85	none
6	16	red-purple	(100)	(100)		85	none
7	20	red-purple	(10) (15) (30)	(4)	(40)	90	none
8	75	green	2 C$_8$ olefins (trace); (100)			60	(structure)
9	77	green	(5) (25) (45)	(25)		90	(structure)

[a] The ratios of the hydrogenation products vary during the course of the reactions. The numbers in parentheses represent approximate percentage yields at >80% conversion.

tigate the mechanism by which carbon fragments bound to more than one metal are converted to paraffins and olefins. We describe here a new method for the synthesis of several (alkylidyne)tricobalt nonacarbonyl and [(alkylidyne)cyclopentadienylmolybdenum]dicobalt octacarbonyl complexes and a study of their hydrogenolysis.[2] Preliminary evidence has been found suggestive of a radical mechanism for the latter process, including the first observation of chemically induced dynamic nuclear polarization (CIDNP) in the reaction of an organometallic cluster complex.

Traditionally, complexes of the form $Co_3(CO)_9CCH_2R$ have been prepared by refluxing dicobalt alkyne complexes $Co_2(CO)_6(HCCR)$ in acidic methanol.[3] We have found that the interaction of metal hydrides, or their equivalent, with those alkyne complexes generates the desired alkylidyne complexes in high yield and purity; this provides a useful alternative in cases where yields in the traditional synthesis are low or workup is difficult. For example, dinuclear cobalt alkyne complex 1, prepared by reaction of $Co_2(CO)_8$ and 3,3-dimethyl-1-butyne, reacted with 3–4 atm of H_2 and $Co_2(CO)_8$ (presumably a source of $HCo(CO)_n$)[4] in a sealed vessel in benzene at 65 °C. After 5 days, filtration, solvent removal, chromatography (hexane/silica), and recrystallization from methanol gave an 80% yield of dark red-purple crystals of tricobalt alkylidyne complex 2 (eq 1). Analogous reactions gave the tricobalt clusters
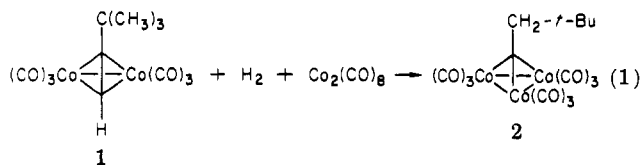
3, 4, and 5 (Table I). Use of $(\eta^5\text{-}C_5H_5)Mo(CO)_3H$ (45 °C, 20 h) in place of H_2 and $Co_2(CO)_8$ led to the mixed cluster 8. Preparation of the double mixed cluster 9 was possible from combination (75 °C, 1 h) of $(\eta^5\text{-}C_5H_5)Mo(CO)_3H$ and

the double acetylene complex formed in the reaction of 1,5-hexadiyne and $Co_2(CO)_8$. Other tricobalt complexes were prepared by known routes. Namely, the phenyl derivative 6 was prepared by the method of Seyferth, Hallgren, and Hung,[5] and reaction of butyl cyclopropyldithiocarboxylate with $Co_2(CO)_8$ in benzene (85 °C, 4 h) yielded the cyclopropylmethylidyne complex 7 (Table I).[6,7]

Reaction of the clusters 2–9 with 3–4 atm of H_2 in benzene leads to the organic products listed in Table I. The products were identified by GC/MS and/or preparative GC followed by ^1H NMR analysis. Though the product distributions vary during the course of the reactions, in most cases the major product is the indicated olefin. In the case of 2 in particular, the loss of starting complex (and the formation of all products) shows first-order dependence on the concentration of 2; the dependence on the pressure of H_2 above the solution has a nonintegral order. However, rates of individual product formation are less well-defined. The ratio of alkene 10 to aldehyde 12 (eq 2) is constant during the hydrogenation
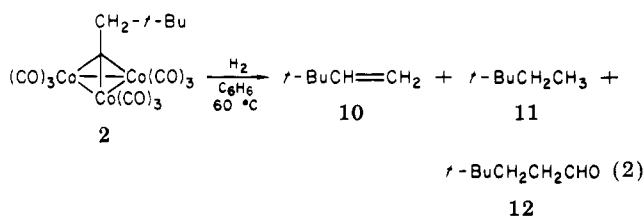
at early reaction times. This suggests that initially 10 and 12 are generated as primary products in concurrent reactions. Later in the reaction, after the concentration of 10 has grown, the concentration of alkane 11 increases rapidly. The rate of production of aldehyde 12 (observed as the ratio ([10] + [11])/[12]) also seems to increase slightly, though the small amounts of this material involved make the change difficult to analyze. These results suggest that secondary reactions of alkene 10 result in conversion of the olefin into the related alkane (by hydrogenation) and aldehyde (by hydroformylation). In aggreement with these conclusions, reaction of alkylidyne complex 2 with H_2 in the presence of added alkene 10 leads to the rapid formation of alkane 11 and aldehyde 12 in excess of that produced in the absence of added 10. Moreover, hydrogenation of 2 in the presence of ethylene gives ethane and propanal as well as 10, 11, and 12.[8]

Further mechanistic information is provided by the fact

(1) See, for example: (a) Shrock, R. R.; Parshall, G. W. *Chem. Rev.* 1976, *76*, 246. (b) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* 1981, *103*, 2488. (c) Mayer, J. M.; Curtis, C. J.; Bercaw, J. E. *Ibid.* 1983, *105*, 2651. (d) San Filippo, J., Jr.; Vitale, A. A. *Ibid* 1982, *104*, 7341. (e) Brintzinger, H. H. *J. Organomet. Chem.* 1979, *171*, 337 and references cited in these papers.

(2) For examples of related studies, see: (a) Geoffroy, G. L.; Epstein, R. A. *Inorg. Chem.* 1977, *16*, 2795. (b) Seyferth, D.; Rudie, C. N.; Nestle, M. O *J. Organomet. Chem.* 1979, *178*, 227. (c) Seyferth, D.; Rudie, C. N.; Merola, J. S. *Ibid.* 1978, *162*, 89. (d) Seyferth, D.; Nestle, M. O.; Eschbach, C. S. *J. Am. Chem. Soc.* 1976, *98*, 6724. (e) Seyferth, D.; Williams, G. H.; Hung, P. L. K.; Hallgren, J. E. *J. Organomet. Chem.* 1974, *71*, 97. (f) Seyferth, D.; Hallgren, J. E.; Hung, P. L. K *Ibid.* 1973, *50*, 265. (g) Fachinetti, G.; Lazzaroni R.; Pucci, S. *Angew. Chem.* 1981, *93*, 1097. (h) Bavaro, L. M.; Montangero, P.; Keister, J. B. *J. Am. Chem. Soc.* 1983, *105*, 4977. (i) Beanan, L. R.; Abdul Rahman, Z.; Keister, J. B. *Organometallics* 1983, *2*, 1062.

(3) For leading reviews on general synthetic methods of (alkylidyne)tricobaltnonacarbonyl complexes, see: (a) Seyferth, D. *Adv. Organomet. Chem.* 1976, *14*, 97. (b) Dickson, R. S.; Fraser, P. J. *Ibid.* 1974, *12*, 323. Also relevant are: (c) Fachinetti, G.; Pucci, S.; Zanazzi, P. F.; Methong, U. *Angew. Chem., Int. Ed., Engl.* 1979, *18*, 619. (d) Dickson, R. S.; Tailby, G. R. *Aust. J. Chem.* 1970, *23*, 229. For methods used in preparing mixed alkylidyne clusters, see: (e) Vahrenkamp, H.; Beurich, H. *Angew. Chem., Int. Ed. Engl.* 1981, *93*, 128. (f) Epstein, R. A.; Withers, H. W.; Geoffroy, G. L. *Inorg. Chem.* 1979, *18*, 942. (g) Chetcuti, M.; Green, M.; Howard, J. A. K.; Jeffrey, J. C.; Mills, R. M.; Pain, G. N.; Porter, S. J.; Stone, F. G. A.; Wilson, A. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* 1980, 1057. (h) Brun, P. Dawkins, G. M.; Green, M.; Mills, R. M.; Salaun, J.; Stone, F. G. A.; Woodward, P. *Ibid.* 1981, 966. (i) Beurich, H.; Vahrenkamp, H. *Chem. Ber.* 1982, *115*, 2385. (j) Beurich, H.; Blumhofer, R.; Vahrenkamp, H. *Ibid.* 1982, *115*, 2409. For an example of use of metal hydrides in the synthesis of other metal clusters, see: (k) Shore, S. G.; Hsu, W.; Weisenberger, C. R.; Caste, M. L.; Churchill, M. R.; Bueno, C. *Organometallics* 1982, *1*, 1405 and references therein.

(4) Penninger, J. M. L.; Alemdarouglu, N. H.; Oltay, E. *Monatsh. Chem.* 1976, *107*, 1043.

(5) Seyferth, D.; Hallgren, J. E.; Hung, P. L. K. *J. Organomet. Chem.* 1973, *50*, 265.

(6) Patin, H.; Mignani, G.; van Hulle, M. *Tetrahedron Lett.* 1979, *26*, 2441.

(7) Data for 2: mp 127–128 °C; IR (benzene) 2095 (m), 2050 (s), 2035 (s), 2010 (m), 1975 (w) cm^{-1}; ^1H NMR (benzene-d_6) δ 3.73 (s, 2 H), 0.98 (s, 9 H). Anal. Calcd for $C_{15}H_{11}Co_3O_9$: C, 35.18; H, 2.17; Co, 34.53. Found: C, 35.49; H, 2.37; Co, 34.50. Data for 3: mp 47–48 °C dec; IR (CCl_4) 2095 (m), 2050 (s), 2035 (s), 2010 (m), 1975 (w) cm^{-1}; ^1H NMR (benzene-d_6) δ 3.75 (s, 2 H), 1.31 (q, 2 H, J = 7.5 Hz), 0.95 (s, 6 H), 0.77 (t, 3 H, J = 7.5 Hz). Anal. Calcd for $C_{16}H_{13}Co_3O_9$: C, 36.53; H, 2.49. Found: C, 36.56; H, 2.55. Data for 7: mp 160–161 °C dec; IR (CCl_4) 2095 (m), 2050 (s), 2035 (s), 2010 (m), 1975 (w) cm^{-1}; ^1H NMR (benzene-d_6) δ 2.51 (m, 1 H), 0.97 (m, 2 H), 0.80 (m, 2 H). Anal. Calcd for $C_{13}H_7Co_3O_9$: C, 32.40; H, 1.04. Found: C, 32.61; H, 1.03. Data for 8: ^1H NMR (benzene-d_6) δ 4.43 (s, 5 H), 4.26 (s, 2 H), 1.18 (s, 9 H). Data for 9: mp >315 °C; IR (benzene) 2060 (m), 2020 (s), 2000 (s), 1945 (m) cm^{-1}; ^1H NMR (benzene-d_6) δ 4.44 (s, 10 H), 4.16 (br t, 4 H, J = 8 Hz), 2.24 (br t, 4 H, J = 8 Hz). Anal. Calcd for $C_{32}H_{18}Co_4Mo_2O_{16}$: C, 35.39; H, 1.67. Found: C, 36.43; H, 1.78. Clusters 4, 5, and 6 were shown to be identical with materials prepared earlier: Cf. ref 5 and (a) Seyferth, D.; Hallgren, J. E.; Spohn, R. J.; Williams, G. H.; Nestle, M. O.; Hung, P. L. K. *J. Organomet. Chem.* 1979, *65*, 99. (b) Seyferth, D.; Williams, G. H.; Hung, P. L. K.; Hallgren, J. E. *Ibid.* 1972, *44*, C55. (c) Seyferth, D.; Hung, P. L. K.; Hallgren, J. E. *Ibid.* 1974, *71*, 97. (d) Seyferth, D.; Eschbach, C. S.; Nestle, M. O. *Ibid* 1975, *97*, C11.

(I)

(II)
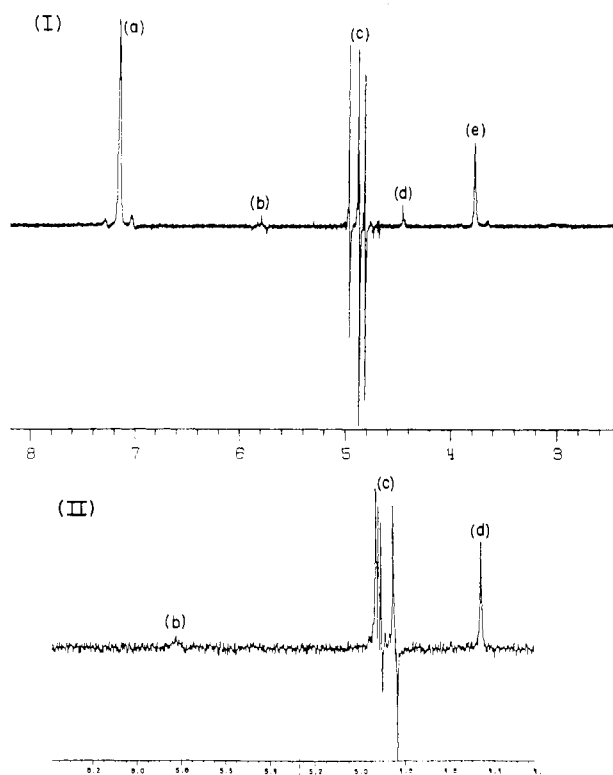
Figure 1. CIDNP observed in ^{1}H NMR during hydrogenolysis reactions of alkylidyne complexes **2** (spectrum I) and **2**-d_2 (spectrum II). Peak identification: (a) residual proton in deuterated benzene solvent; (b) internal vinyl hydrogen in 3,3-dimethyl-1-butene product; (c) terminal vinyl hydrogens; (d) dissolved H_2; (e) CH_2 hydrogens in starting alkylidyne complex. Scale is in δ units, ppm downfield from tetramethylsilane internal standard.

that carbon monoxide strongly inhibits the reaction of **2** with hydrogen.[9] In the presence of a 50/50 (mol/mol) mixture of CO/H_2, heating to 85 °C is required to give slow production of aldehyde **12** as the sole product. Moreover, treatment of **2** with both triethylphosphine and H_2 at 25 °C results in rapid incorporation of 3 equiv of PEt_3 into the cluster long before any hydrogenation takes place,[10] while hydrogenation under tetrafluoroethylene[11] has no influence on the reaction. This indicates that hydrogenation of **2** involves initial dissociative CO loss.

The most striking observation in these hydrogenolyses is the occurrence of CIDNP in the products from some of the trinuclear clusters. When a sample of **2, 3,** or **8** is heated under 3–4 atm of H_2 in an NMR probe at 60 °C, CIDNP due to the vinyl proton signals of the alkene being produced is observed in the ^{1}H NMR spectra taken throughout the reaction. Hydrogenation of compound **9** leads to weak polarization in the terminal vinyl protons of only the 1-hexene produced. Hydrogenolysis of **2** or **3** with D_2 gave no proton CIDNP signals, while reaction of $Co_3(CO)_9CCD_2C(CH_3)_3$ (**2**-d_2) with H_2 gave a new olefinic

CIDNP pattern attributable to t-BuCDCH$_2$. Figure 1 illustrates the CIDNP observed during hydrogenolysis of **2** and **2**-d_2.

The observation of CIDNP signals requires that at least some of the alkene product is formed in a reaction involving radicals. The CIDNP and labeling evidence discussed below suggests that *tert*-butylvinyl radicals are the specific intermediates involved. In an attempt to trap these radicals, the reaction of **2**-d_2 with D_2 was carried out in the presence of the following hydrogen atom donors: dihydroanthracene, diphenylmethane, and triphenylmethane. The resulting 3,3-dimethyl-1-butene was analyzed for hydrogen content by ^{1}H NMR and GC/MS. The largest amount of incorporation was found to be 13% for dihydroanthracene and was independent of trapping agent concentration. The alkene formed was 10-d_2, as determined by GC/MS. This suggests that virtually all of the *tert*-butylvinyl radicals that escape the cage containing the second radical are being trapped and is consistent with the limited cage escape necessary for the observation of CIDNP.

Data consistent with a radical mechanism for cleavage of the organic moiety from these trinuclear alkylidyne compounds is also provided in the hydrogenolysis of cyclopropylmethylidyne complex **7** (Table I). No cyclopropyl-containing products are observed in the hydrogenolysis of **7**, and a control experiment demonstrated that methylcyclopropane is stable to the reaction conditions. This is consistent with the production of cyclopropylcarbinyl radical as an intermediate, which is known to very rapidly rearrange to the homoallylic radical (eq 3),[12] ac-

$$\triangleright\!\!-\!\overset{\bullet}{C}H_2 \;\xrightarrow{\;\;}\; H_2\overset{\bullet}{C}\!-\!CH_2\!-\!CH=\!CH_2 \qquad (3)$$
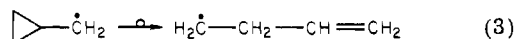
counting for the formation of the butenes and butane. It is intriguing that cyclopentanone is also produced in this reaction; we hope to uncover the pathway by which it is formed.

It is clear from this work that radicals are involved in the process that leads to the observed hydrogenolysis products. We presume this reaction is initiated by CO dissociation from one metal center, followed by H_2 oxidative addition and cleavage, by reductive elimination, of metal–carbon bonds in the cluster. This could lead to an intermediate (perhaps a bi- or trinuclear σ-vinyl complex) which fragments to a cage containing a vinyl radical and reactive metal hydride. This species could undergo cage escape, leading to free radicals, or hydrogen transfer to give polarized alkene product. Further studies are underway aimed at developing a more specific mechanistic picture and simulating accurately the observed CIDNP spectra. In any case, this is the first organometallic cluster reaction for which CIDNP has been detected. Our results suggest that radicals should be considered as viable intermediates in other metal–carbon bond cleavage reactions of clusters, and perhaps of surfaces as well.

(8) We do not necessarily believe **2** itself is the catalyst for olefin hydrogenation or hydroformylation. See: Ryan, R. C.; Pittman, C. U.; O'Connor, J. P. *J. Am. Chem. Soc.* **1977**, *99*, 1986.

(9) We believe it is this property which allows synthesis of the tricobalt alkylidyne clusters at 65 °C; the CO lost from $Co_2(CO)_8$ during the reaction inhibits the hydrogenolysis. Carbon monoxide also retards the conversion of $Co_2(CO)_8$ to $Co_4(CO)_{12}$.

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(μ-Bicarbonato)bis(μ-methylene)bis(pentamethyl-cyclopentadienyl)dirhodium Tetrafluoroborate (Synthesis and X-ray Structure) and Related Complexes

Neil J. Meanwell, Arnold J. Smith, Harry Adams, Seichi Okeya, and Peter M. Maitlis*

Department of Chemistry, The University
Sheffield S3 7HF, England

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Summary: Reaction of *trans*-[(C_5Me_5Rh-μ-CH_2)_2Cl_2] with Na_2CO_3 gives the *cis*-μ-carbonato complex [(C_5Me_5Rh-μ-CH_2)_2CO_3]. This is protonated in acid to give the *cis*-μ-bicarbonato salt [(C_5Me_5Rh-μ-CH_2)_2HCO_3]BF_4, characterized by an X-ray structure determination; with more acid, CO_2 is lost to give the trans-diaqua dication [(C_5Me_5Rh-μ-CH_2)_2(H_2O)_2]^{2+}. The ¹H NMR spectra show the methylene bridges to be retained throughout these transformations.

We have noted on several occasions the ability of pentamethylcyclopentadienyl, when attached to rhodium, of stabilising bonds to formally hard ligands such as oxygen donors.[1-7] This may be related to the ability of C_5Me_5Rh to support ligands in complexes of unusually high oxidation states, e.g., Rh(IV)[8] or Rh(V).[9,10] Presumably this is because the C_5Me_5 ligand can act as a very effective electron reservoir and can thus respond to high electronic demand by the metal and the other ligands.

We here report that the dichlorobis(μ-methylene)dirhodium(IV) complex (1)[11] reacted readily with an excess of sodium carbonate in methanol (30 min, 20 °C) to give the yellow neutral *cis*-(μ-carbonato)bis(μ-methylene)dirhodium complex (2) in 79% yield, after crystallization
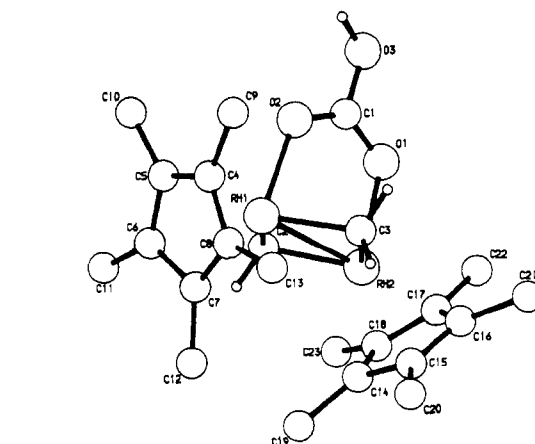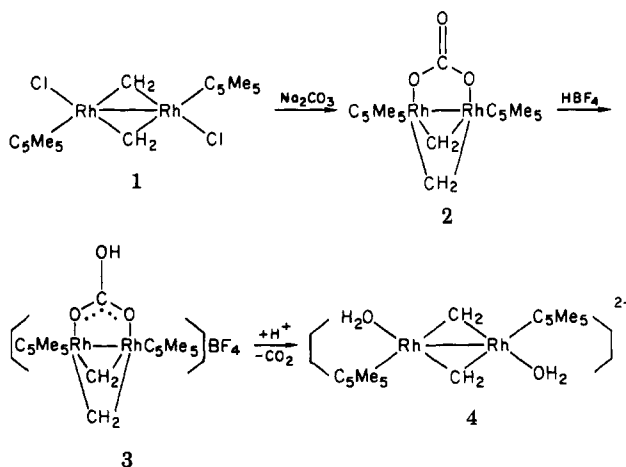

Figure 1.

from cold benzene. Complex 2 also dissolved in water; on addition of concentrated fluoroboric acid to an aqueous solution of 2 pale orange crystals of *cis*-(μ-bicarbonato)-bis(μ-methylene)bis(pentamethylcyclopentadienyl)dirhodium tetrafluoroborate hydrate (3) precipitated in 44% yield. The complexes were identified by microanalysis[13] and spectroscopically.[14] The ¹H NMR spectrum in particular showed the characteristic pattern, of a higher field doublet and a lower field multiplet, for the diastereotopic μ-CH_2 resonances in a cis complex.[8]

A single-crystal X-ray determination was carried out on 3 to show the structure indicated in Figure 1.[15] The complex has two rhodiums, each η^5 bonded to a C_5Me_5 (mean Rh–C = 2.187 Å) and σ bonded to the two methylene carbons (mean Rh–C = 2.00 Å). They are also bridged by a somewhat asymmetrically bonded bicarbonate ligand

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(11) Readily obtained by reaction of *trans*-[(C_5Me_5RhMe)_2(μ-CH_2)_2][8] with HCl in pentane.[12]

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(13) Anal. Calcd for $C_{23}H_{34}O_3Rh_2$ (2): C, 49.0; H, 6.1. Found C, 50.6; H, 6.3. Calcd for $C_{23}H_{37}BF_4O_4Rh$ (3): C, 41.2; H, 5.6. Found: C, 40.8; H, 5.7.

(14) IR: 1530 (s), 1544 (sh) (2) and 1572 (m), 1555 (sh) (3) cm⁻¹ are associated with the coordinated CO_3. 2: ¹H NMR (CDCl_3) δ 1.69 (s, C_5Me_5), 9.06 [d, CH_2, H_{ax}, J(H–H) = 3 Hz] and 9.52 [m, CH_2, H_{eq}, J(H–H) = 3, J(Rh–H) = 2 Hz]. 3: ¹H NMR (CDCl_3) δ 1.69 (s, C_5Me_5), 3.79 (s, br, H_2O), 9.08 (d, CH_2, H_{ax}, J(H–H) = 2.5 Hz) and 9.52 (m, CH_2, H_{eq}, J(H–H) = 2.5, J(Rh–H) = 2 Hz].

(15) Crystal data: [C_{23}H_{35}O_3Rh_2]BF_4·H_2O, M_r = 670; monoclinic; a = 28.82 (3) Å, b = 8.803 (5) Å, c = 20.36 (2) Å, β = 93.86 (8)°; U = 5157 Å³; Z = 8; D_{measd} = 1.73, D_{calcd} = 1.73 g cm⁻³; $F(000)$ = 2703; space group C2/c; Mo Kα radiation (λ = 0.710 69 Å); μ = 13.14 cm⁻¹. X-ray data collected (3.5° ≤ 2θ ≤ 47°) on Nicolet R3M four-circle diffractometer to give 2030 independent reflections ($I \geq 4\sigma(I)$). Structure solved and refined by using SHELXTL programs to R = 0.061. The BF_4⁻ is disordered, and the water molecule (not shown) is hydrogen bonded to the bicarbonate and the BF_4⁻.