Carbon13 nuclear magnetic resonance of pentadecacarbonylcarbylhexarhodate(2-)

(13) Studies on model compound i confirmed that the epoxidation was highly stereoselective with the angular methyl group having a very large influ-

ence on the steric course of the reaction. The nmr chemical shifts of the angular methyl groups and the splitting patterns of the methine protons supported our stereochemical assignments.
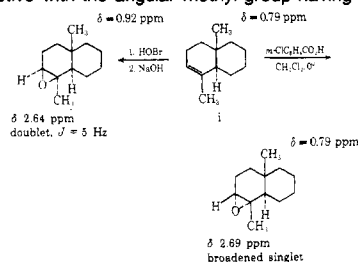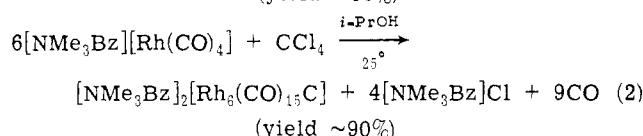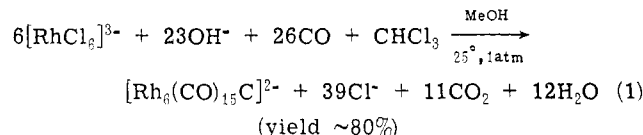
(14) B. Rickborn and R. P. Thummel, J. Org. Chem., **34**, 3583 (1969); J. Amer. Chem. Soc., **92**, 2064 (1970); J. Org. Chem., **36**, 1365 (1971); **37**, 3919, 4250 (1972); C. L. Kissel and B. Rickborn, ibid., **37**, 2060 (1972).
(15) For some related cases, see (a) J. A. Marshall and N. Cohen, J. Amer. Chem. Soc., **87**, 2773 (1965); (b) A. Minato and I. Horibe, Chem. Commun., **531** (1965); (c) G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrel, J. Amer. Chem. Soc., **85**, 207 (1963).
(16) H. O. House, H. Babad, R. B. Toothill, and A. W. Noltes, J. Org. Chem., **27**, 4141 (1962).
(17) See Experimental Section of ref 16; J. I. Musher, J. Amer. Chem. Soc., **83**, 1146 (1961).

Communications to the Editor

^{13}C Nuclear Magnetic Resonance of $[Rh_6(CO)_{15}C]^{2-}$

Sir:

The carbide atom in transition metal carbonyl cluster carbides has been claimed to result from two different sources: bonded carbon monoxide is believed to disproportionate to carbon and carbon dioxide,[1] and, recently, halocarbons such as $CHCl_3$[2] and CCl_4 have been found to be the source of the carbide atom, according to the reactions

$$6[RhCl_6]^{3-} + 23OH^- + 26CO + CHCl_3 \xrightarrow[25°,1atm]{MeOH}$$

$$[Rh_6(CO)_{15}C]^{2-} + 39Cl^- + 11CO_2 + 12H_2O \quad (1)$$
$$(\text{yield} \sim 80\%)$$

$$6[NMe_3Bz][Rh(CO)_4] + CCl_4 \xrightarrow[25°]{i\text{-}PrOH}$$

$$[NMe_3Bz]_2[Rh_6(CO)_{15}C] + 4[NMe_3Bz]Cl + 9CO \quad (2)$$
$$(\text{yield} \sim 90\%)$$

Although we have observed that in both cases the carbide cluster is not obtained in the absence of the halocarbon, in view of the novelty of these syntheses we wished to have unequivocal proof of the source of the carbide atom in the $[Rh_6(CO)_{15}C]^{2-}$ dianion. To this end we have synthesized $[Rh_6(CO)_{15}{}^{13}C]^{2-}$ (ca. 90% ^{13}C) starting from $^{13}CCl_4$ and the $[Rh(CO)_4]^-$ anion, and the ^{13}C nmr spectrum of this species has been recorded in perdeuterioacetone solution containing $Cr(acac)_3$ as relaxing agent.[3] The resonance of the carbide carbon should show a septet pattern due to coupling with six equivalent rhodium atoms. Both at room temperature and at $-70°$, the spectrum (Figure 1a) shows a symmetrical five-line pattern and it seems probable that the outer lines of the expected septet are not resolved since the relative intensities of the five lines, 8.6:15.7:20.0:15.2:8.4, show better agreement with the relative intensities of a septet rather than a quintet pattern. The spacing between the lines is 13.7 ± 2 Hz and this low value of $^1J(Rh-C_D)$ (see Figure 2) is consistent with the expected low s character of the rhodium–carbide bonds. The carbide resonance (264.7 ppm)[4] occurs at very low field and is in the region found for carbonium ions[5] and rhodium carbene complexes.[6] The shortness of the carbide radii in similar clusters of ruthen-

ium[7] and iron[8] is in favor of a positive and contracted carbide atom.

^{13}CO interexchange with $[Rh_6(CO)_{15}C]^{2-}$ occurs very slowly at room temperature and atmospheric pressure. At 80° (in tetrahydrofuran solution) exchange is faster, but decomposition to give uncharacterised species also takes place. However, under these last conditions we were able to
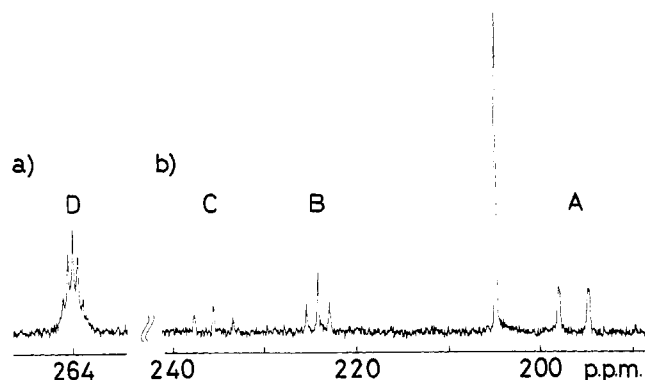

Figure 1. The ^{13}C nmr spectrum of (a) $[Rh_6(CO)_{15}{}^{13}C]^{2-}$ (ca. 90% ^{13}C) and (b) $[Rh_6(CO)_{15}C]^{2-}$ (ca. 42% ^{13}CO) at $-70°$ in perdeuterioacetone solution in the presence of $Cr(acac)_3$.
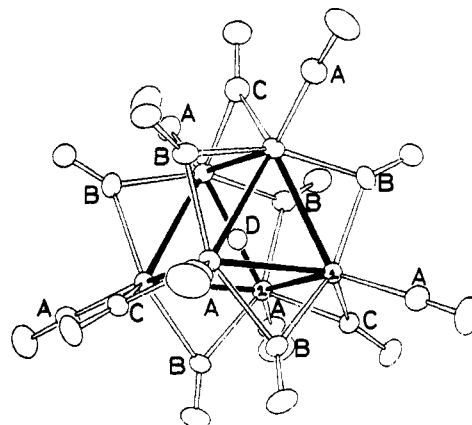

Figure 2. The X-ray structure of $[Rh_6(CO)_{15}C]^{2-}$.[2]

introduce $18.5 \pm 1\%$ of ^{13}CO into $[Rh_6(CO)_{15}C]^{2-}$. The ^{13}CO-enriched complex, $[Rh_6(CO)_{15}C]^{2-}$ $(42 \pm 1\%$ $^{13}CO)$ was also prepared from CCl_4 and ^{13}CO-enriched $[Rh(CO)_4]^-$ (δ 206.33 ppm, $^1J(Rh-C)$ 74.7 ± 1 Hz). In both cases the ^{13}C nmr spectra at -70 and $+25°$ were similar (see Figure 1b) and showed the absence of the carbide resonance at 264.7 ppm.

The inequivalent bridging carbonyls both appear as triplets (B, δ 225.2 ppm, $^1J(Rh-C)$ 30.8 ± 2 Hz; C, δ 236.3 ppm, $^1J(Rh-C)$ 51.8 ± 2 Hz) whereas the terminal carbonyl resonance (δ_A 198.1 ppm) is a doublet of doublets, which we believe is due to $^1J(Rh_1-C_A)$ 77.1 ± 2 Hz and $^2J(Rh_2-C_A)$ 3.9 ± 2 Hz (see Figure 2).[9]

In all the above cases the values of the chemical shifts for the carbonyl resonances are similar to those recently reported for related compounds,[10] and generally an increase in rhodium–carbon bond length results in a decrease in $^1J(Rh-CO)$.

Acknowledgments. We thank the Royal Society and the Accademia dei Lincei for postdoctoral fellowships (D.J.A.McC. and D.S. respectively), NATO for a grant, Dr. P. R. Mitchell for a gift of the $^{13}CCl_4$, and D. O. Smith for recording the ^{13}C nmr spectra.

References and Notes

(1) C. R. Eady, B. F. G. Johnson, J. Lewis, and T. Matheson, *J. Organometal. Chem.*, **57**, C82 (1973).
(2) V. G. Albano, M. Sansoni, P. Chini, and S. Martinengo, *J. Chem. Soc., Dalton Trans.*, 651 (1973).
(3) O. A. Gansow, A. R. Burke, and G. N. LaMar, *J. Chem. Soc., Chem. Commun.*, 456 (1972).
(4) Chemical shifts (downfield positive) are quoted with respect to internal Me₄Si throughout this communication.
(5) J. B. Stothers, "Carbon-13 N.M.R. Spectroscopy," Academic Press, New York, N.Y., 1973, pp 217–237.
(6) T. Yamamoto, A. R. Garber, J. R. Wilkinson, C. B. Boss, W. E. Streib, and L. J. Todd, *J. Chem. Soc., Chem. Commun.*, 354 (1974); P. R. Bronson, R. A. Cable, M. Green, and M. K. Lloyd, *ibid.*, 364 (1974).
(7) R. Mason and W. R. Robinson, *J. Chem. Soc., Chem. Commun.*, 468 (1968).
(8) M. R. Churchill, J. Wormald, J. Knight, and M. J. Mays, *J. Amer. Chem. Soc.*, **93**, 3073 (1971).
(9) Although we presently favor this assignment, a referee has pointed out that the assignment of 3.9 ± 2 Hz to a single parameter is unlikely in view of the complexity of the spin system.
(10) P. Chini, S. Martinengo, D. J. A. McCaffrey, and B. T. Heaton, *J. Chem. Soc., Chem. Commun.*, 310 (1974), and references therein.

**Vincenzo G. Albano, Paolo Chini,* Secondo Martinengo
David J. A. McCaffrey, Donatella Strumolo**

*Istituto di Chimica Generale ed Inorganica dell'Università
20133 Milan, Italy*

**Brian T. Heaton**

University of Kent, Canterbury, England

Sterol Biosynthesis from (3RS, 2R)-[2-^{14}C,2-^{3}H]-Mevalonic Acid in a Yeast Homogenate. Stereochemistry of the C-15 Tritium Atom[1,2]

Sir:

Several years ago we described significant stereochemical differences in the elaboration of sterols by rat liver[3] and by yeast[4] enzymes. These observations were made during the investigation of the biosynthesis of sterols from (3RS,2R)-[2-^{14}C,2-^{3}H]mevalonic acid (MVA) and (3RS,2S)-[2-^{14}C,2-^{3}H]MVA by a cell free yeast preparation.[4] It was noticed that in this enzyme system *essentially only* C_{27} sterols were formed and that usually major amounts of radioactivity were incorporated[5,6] into cholesta-5,7,24-trien-3β-ol (1) and 5α-cholesta-7,24-dien-3β-ol (2). The (R)-1a and
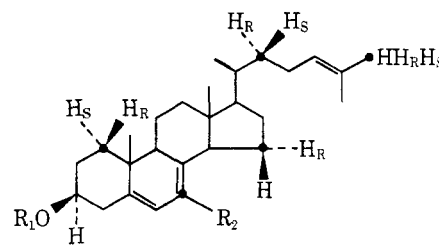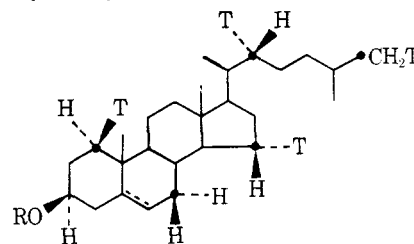

1a, $R_1 = H$; $R_2 = H$; $H_R = T$
b, $R_1 = H$; $R_2 = T$; $H_S = T$
c, 1a acetate
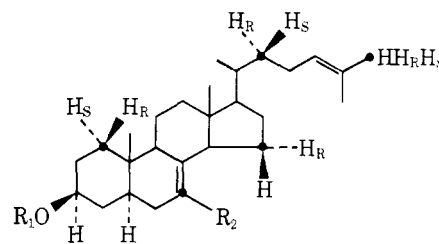
2a, $R_1 = H$; $R_2 = H$; $H_R = T$
b, $R_1 = H$; $R_2 = T$; $H_S = T$
c, 2a acetate
d, $R_1 = H$; $R_2 = H$; $H_R = T$ no Δ^{24}

● Carbon atoms derived from C-2 of MVA (^{14}C); T = ^{3}H; H_R and H_S refer to 2 pro R and 2 pro S hydrogens of MVA, respectively.

3a, $R = H$; Δ^5
b, $R = Ac$; Δ^5
c, $R = Ac$; no Δ^5, $5\alpha(H)$

(R)-2a as well as (S)-1b and (S)-2b each retained four atoms of tritium and five atoms of ^{14}C.[4-6] We have proven[4] that (R)-1a and (R)-2a were *devoid* of tritium atoms at C-7 while the (S)-1b and (S)-2b *retained* tritium atoms at C-7. This observation was in sharp contrast to the situation in rat liver systems[3] in which the transformation of the $\Delta^{8(9)}$ sterol to the Δ^7 isomer proceeds with the loss of a hydrogen derived from 2 pro S of MVA.

It was deduced[4-6] that the yeast (S) metabolites had tritium atoms at C: 1α,7,22, and 26. The (R) metabolites[4-6] had tritium atoms at C: 1β,22 and 26. This left one isotopic hydrogen unaccounted for which was likely to be located[4,12] at C-15. We therefore undertook to determine the location and the stereochemistry of the "fourth" tritium atom of the (R) metabolites.

The homogenate was prepared from aerobically grown yeast as previously reported.[6] The (3RS,2R)-[2-^{14}C,2-^{3}H]MVA (18 μCi of ^{14}C; ^{3}H: ^{14}C ratio 10.7) was incubated[6] with an aliquot of the homogenate corresponding to 1.5 g of wet cells under an atmosphere of O_2. After conventional work-up[6] the nonsaponifiable residue (1.32 × 10^7 dpm of ^{14}C) was acetylated and resolved into homogeneous trien-acetate (1c) (8.7 × 10^4 dpm) and dien–acetate (2c) (1.06 × 10^6 dpm of ^{14}C). Hydrogenation[7] (EA; Raney-Ni) of a mixture of 2c (4.8 × 10^4 dpm of ^{14}C) and cholesta-5,7-dien-3β-ol acetate resulted in[$^{14}C_5$;$^3H_4$]-5α-cholest-7-en-