

Metal-Carbonyl Syntheses. 9.¹ Carbon Monoxide—A Six-Electron Ligand? Synthesis and Structural Characterization of the Unusual Carbonylniobium Cluster ($\eta^5\text{-C}_5\text{H}_5$)₃Nb₃(CO)₇

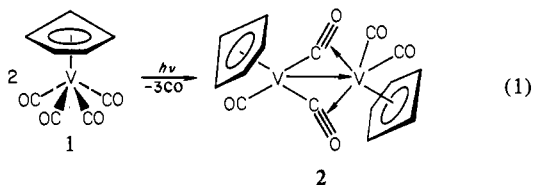
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Abstract: The "half-sandwich" complex tetracarbonyl(η^5 -cyclopentadienyl)niobium, ($\eta^5\text{-C}_5\text{H}_5$)Nb(CO)₄ (**3**), is converted into a novel crystalline cluster compound of composition ($\eta^5\text{-C}_5\text{H}_5$)₃Nb₃(CO)₇ (**4**) upon photolysis in hexane solution at +18 °C. The trinuclear complex **4** not only represents the first carbonyl niobium cluster reported to date but also exhibits an unprecedented type of carbon monoxide coordination: X-ray diffraction techniques reveal one of the seven CO ligands to act as a η^2 ($\mu_3\text{-C}, \mu_2\text{-O}$) bridge symmetrically facing a nearly equilateral niobium triangle. This unusual mode of coordination causes a dramatic lengthening of the respective C—O distance (130.3 (14) pm) as compared to well-behaved terminal carbonyl groups (108–117 pm) accompanied by a long-wave shift of the corresponding $\nu(\text{CO})$ absorption, the latter being observed at 1330 cm⁻¹ (KBr). The molecular origin of CO triply semibringing is interpreted in terms of neutralization of unequal charge distribution in the asymmetric molecule rather than by steric pressures. Exhausting its bonding capacity, the unique carbon monoxide ligand thus acts as a six-electron ligand toward a total of three metal centers.

Introduction

Our interest in di- and polynuclear carbonyl complexes of the early transition-metal series stems from both their synthetic challenge which has greatly attracted our preparative efforts and their potential for serving as models for the catalytic hydrogenation of carbon monoxide—a process which we are trying to approach along the stoichiometric paths starting from transition-metal methylene complexes as well.^{4,5} Preceding experiments have demonstrated⁶ that photolysis of the well-known "half-sandwich" complex ($\eta^5\text{-C}_5\text{H}_5$)V(CO)₄ (**1**) provides a straightforward route to the dinuclear derivative ($\eta^5\text{-C}_5\text{H}_5$)₂V₂(CO)₅ (**2**) (eq 1)⁷ which,



in turn, represents a remarkable prototypal example in which the so-called "semibringing" type of carbon monoxide coordination was recognized and interpreted by Cotton and his group.^{8,9}

(1) Communication 8: W. A. Herrmann, H. Biersack, M. L. Ziegler, and B. Balbach, *J. Organomet. Chem.*, in press.

(2) (a) Universität Regensburg. (b) Universität Heidelberg. (c) Universität Hamburg.

(3) Karl Winnacker Scholarship Recipient, 1979–1984.

(4) (a) W. A. Herrmann, C. Krüger, R. Goddard, and I. Bernal, *J. Organomet. Chem.*, **140**, 73 (1977). (b) W. A. Herrmann, J. Plank, D. Riedel, M. L. Ziegler, M. Guggolz, and B. Balbach, *J. Am. Chem. Soc.*, **103**, 63 (1981).

(5) W. A. Herrmann and J. Plank, *Angew. Chem.*, **90**, 555 (1978); *Angew. Chem., Int. Ed. Engl.*, **17**, 525 (1978).

(6) W. A. Herrmann and J. Plank, *Chem. Ber.*, **112**, 392 (1979).

(7) (a) E. O. Fischer and R. J. J. Schneider, *Angew. Chem.*, **79**, 537 (1967); *Angew. Chem., Int. Ed. Engl.*, **6**, 569 (1967); (b) *Chem. Ber.*, **103**, 3684 (1970).

(8) F. A. Cotton, *Prog. Inorg. Chem.*, **21**, 1 (1976), and references cited therein. Historically seen was the ferrole complex $\text{Fe}_2(\mu\text{-CO})(\text{CO})_5\text{[CH}_2\text{C}_2(\text{COH})_2]$, the very first example in which semibringing CO's were reliably detected: A. A. Hock and O. S. Mills, *Acta Crystallogr.*, **14**, 139 (1961).

The light-induced synthesis of **2** as well as the thermal dismutation of the latter, yielding organometallic clusters of composition ($\eta^5\text{-C}_5\text{H}_5$)₄V₄(CO)₄ and ($\eta^5\text{-C}_5\text{H}_5$)₃V₃(CO)₉¹⁰ called for an investigation of the chemistry of the heavier homologues ($\eta^5\text{-C}_5\text{H}_5$)Nb(CO)₄ and ($\eta^5\text{-C}_5\text{H}_5$)Ta(CO)₄, respectively. After we had cleared away a serious obstacle concerning the poor synthetic availability of the niobium compound **3**, by designing high-pressure syntheses for the latter,^{11,12} we also succeeded in the preparation and structural characterization of some novel hydrido and sulfur derivatives.^{13,14} This paper gives a full-length account of the synthesis, spectroscopy, and crystal structure of the unexpected carbonylniobium cluster having the curious stoichiometry ($\eta^5\text{-C}_5\text{H}_5$)₃Nb₃(CO)₇. A preliminary communication has appeared in 1979.¹⁵

Experimental Section

General Data. All manipulations were carried out under rigorous exclusion of air and moisture (absolutely dry-nitrogen atmosphere, Schlenk-tube technique). All solvents (reagent grade) were distilled over sodium-potassium alloy (aliphatic hydrocarbons, benzene, diethyl ether, tetrahydrofuran; benzophenone as H₂O/O₂ indicator), phosphorus pentoxide (methylene chloride), and activated molecular sieves (acetone; Merck, 3 A), respectively, and were stored under an atmosphere of dry nitrogen. Oven-dried glassware was repeatedly evacuated on a high-speed pumping system (Edwards ED-3) and subsequently filled with nitrogen prior to use. Elemental analyses were performed in the Mikroanalytisches Laboratorium der Universität Regensburg and in the Analytische Laboratorien, vorm. A. Bernhardt, Gummersbach/Elbach, West Ger-

(9) (a) F. A. Cotton, B. A. Frenz, and L. Kruczynski, *J. Am. Chem. Soc.*, **95**, 951 (1973); (b) *J. Organomet. Chem.*, **160**, 93 (1978).

(10) W. A. Herrmann, J. Plank, and B. Reiter, *J. Organomet. Chem.*, **164**, C25 (1979).

(11) W. A. Herrmann and H. Biersack, *Chem. Ber.*, **112**, 3942 (1979).

(12) W. A. Herrmann and H. Biersack, *J. Organomet. Chem.*, **191**, 397 (1980); *ibid.*, **195**, C24 (1980). Note that the synthetic route described in this paper cannot be extended to the synthesis of the homologous tantalum compound ($\eta^5\text{-C}_5\text{H}_5$)Ta(CO)₄; cf. E. Guggolz, M. L. Ziegler, H. Biersack, and W. A. Herrmann, *J. Organomet. Chem.*, **194**, 317 (1980).

(13) W. A. Herrmann, H. Biersack, M. L. Ziegler, and P. Wülknitz, *Angew. Chem.*, in press.

(14) J. A. Labinger and W. A. Herrmann, et al., in preparation.

(15) W. A. Herrmann, M. L. Ziegler, K. Weidenhammer, and H. Biersack, *Angew. Chem.*, **91**, 1026 (1979); *Angew. Chem., Int. Ed. Engl.*, **18**, 960 (1979).

many. Melting and decomposition points respectively were taken in sealed capillaries on a Büchi melting point apparatus, SMP-20 (heating speed ca. 3 °C/min).

Tetracarbonyl (η^5 -cyclopentadienyl)niobium (**3**) was synthesized in approximately 50-g amounts from $(\eta^5\text{-C}_5\text{H}_5)\text{NbCl}_4$ by high-pressure carbonylation according to the procedure recently developed in our laboratory¹² and was purified by column chromatography and subsequent crystallization. Photolyses of **3** were carried out in a cylindrical Schlenk tube (diameter 5.0 cm; length 22.0 cm; Duranglass) equipped with an external cooling mantle which was connected to an external cooling device (HAAKE cryostat, type KT 33; coolant, methanol). The top of the reaction vessel was fitted with a mercury-filled pressure-relief valve. ^{13}C - and $^{13}\text{C}^{18}\text{O}$ -enriched samples of $(\eta^5\text{-C}_5\text{H}_5)\text{Nb}(\text{*C}^{18}\text{O})_4$ (**3**) were prepared as described previously.¹²

Spectroscopy. Infrared spectra were obtained by employing a Beckman grating spectrophotometer, type 4240; band positions were accurate within $\pm 1\text{ cm}^{-1}$. Field-desorption mass spectra were recorded on a Varian 311-A high-resolution spectrometer. No electron-impact mass spectra (Varian CH 5) could be obtained from the cluster compounds **4-6**. ^1H and ^{13}C NMR spectra were recorded on a Bruker WH-90 spectrometer. The ^{13}C NMR spectrum of **4** was taken from a ca. 20% ^{13}C -enriched sample.

Preparation of $[\eta^2(\mu_3\text{-C}, \mu_2\text{-O})\text{-Carbonyl}]\text{tris}[\text{dicarbonyl}(\eta^5\text{-cyclopentadienyl)niobium}](3\text{Nb-Nb})$ (4**).** A solution of 2.70 g (10.0 mmol) **3** in 250 mL of hexane is exposed, without agitation, to bright sunlight for a period of at least 15 h while the reaction temperature is kept at exactly 18.0 °C. After a short while, dark black lustrous needles which are sometimes 1.5 cm in length begin to separate from the solution; at the same time, carbon monoxide slowly bubbles out of the vessel through the pressure-relief valve. Since the crystalline product not only separates at the bottom of the flask but also grows along the walls, it has to be removed occasionally by carefully shaking the Schlenk tube for a few seconds. It is to be noted that photolysis of **3** by the action of sunlight was found to be the cleanest and easiest method of obtaining crystalline and absolutely pure samples of the niobium cluster **4**. Use of both conventional immersion-well apparatus and falling-film photoreactors¹⁶ operating with artificial light sources (mercury high-pressure lamps) was repeatedly found to merely give powdery, amorphous, brown products which are not analytically pure. Moreover, purification of the latter rendered cumbersome and difficult since column chromatography on silica or florisil fails in this case. Therefore, reliable spectral information is only obtained from crystalline samples. On the other hand, if one has once produced crystalline **4** under the reaction conditions described above, the compound easily recrystallizes from methylene chloride/diethyl ether in the temperature range between -15 and -35 °C; we have succeeded in growing big shining cubes (5 × 5 × 5 mm) by this means but have been unsuccessful in obtaining good-quality crystals from a powdery crude product. The reaction period depends upon the light intensity. During a sunny day, some 50–70% of the starting material is converted to **4**. The product is collected by decantation after most of the starting complex seems to be consumed. The supernatant solution is filtered (D3 frit) and again exposed to sunlight until the conversion of $(\eta^5\text{-C}_5\text{H}_5)\text{-Nb}(\text{CO})_4$ (**3**) to $(\eta^5\text{-C}_5\text{H}_5)_3\text{Nb}_3(\text{CO})_7$ (**4**) has gone to completion which takes another 15–80 h.

The crystalline cluster **4** thus obtained in 65–82% yield is washed several times with hexane and finally dried in a high vacuum for a few hours at close to ambient temperatures. Note that the yield is based solely upon crystalline product; the gross yield is close to 100%, with sufficiently long irradiation provided. A minor amount (20–25%) of fluffy, amorphous **4** which comes along with the crystalline product is easily removed with the mother liquor upon decantation of the latter during the isolation of **4**. We have also extended this procedure to far greater amounts of **3** by using bigger reaction vessels; the yields obtained for **4** remained essentially the same.

Anal. Calcd for $\text{C}_{22}\text{H}_{15}\text{Nb}_3\text{O}_7$ (670.1): C, 39.43; H, 2.26; N, 0.00; Nb, 41.59. Found: C, 39.46; H, 2.11; N, 0.00; Nb, 41.54. Molecular weight 670 (field-desorption mass spectrum; acetone; $I_{\text{EM}} = 0.1\text{ mA}$; $U_{\text{EM}} = 3.1\text{ kV}$; I (filament) = 20–25 mA; SEM = 3.5 kV; $T = 110\text{ °C}$, $p < 10^{-7}$ torr).

$(\eta^5\text{-C}_5\text{H}_5)_3\text{Nb}_3(\text{CO})_7$ (**4**) forms black lustrous needles that slowly begin to decompose in a sealed capillary above ca. 100 °C with partial formation of the mononuclear precursor **3**. The compound can be handled in open air for at least 20 min without any noticeable decomposition (monitored by IR and ^1H NMR spectroscopy as well as by C and H analyses). **4** is very soluble and stable in methylene chloride, tetrahydrofuran, and acetone and moderately soluble in benzene and diethyl

Table I. Infrared Data ($\nu(\text{CO})$, cm^{-1}) of the Niobium Cluster **4** and Its Labeled Derivatives **5** and **6**

| | |
|----------------|---|
| 4 | 1993 w m, 1973 vs, 1952 w, 1934 m, 1907 s (cyclohexane) |
| | 1982 s vs, 1961 vs, 1947 vs, 1915 vs, 1885 s, 1850 s vs, 1838 s, 1330 w m (KBr) ^a |
| | 1994 m, 1971 vs, 1952 m, 1931 s, 1904 vs (diethyl ether) |
| | 1992 m s, 1969 vs, 1950 m s, 1930 s vs, 1902 vs (CS_2) |
| 5 ^b | 1993 m s, 1970 vs, 1925 s, 1902 s (CH_2Cl_2) |
| | 1990 m s, 1963 vs, 1926 s vs, 1898 vs (C_6H_6) |
| | 1990 m, 1968 vs, 1946 m, 1924 m s, 1899 m s (THF) |
| | 1992 m, 1971 vs, 1958 s, 1932 s, 1905 s vs, 1877 m s (^{13}C) (cyclohexane) |
| 6 ^b | 1979 s, 1957 s vs, 1946 s vs, 1914 s vs, 1884 s, 1848 s, 1811 sh, 1330 m, 1296 w m (KBr) |
| | 1990 m, 1968 vs, 1955 s (^{13}C), 1929 s vs, 1902 vs, 1874 s (^{13}C) (CS_2) |
| | 1992 s, 1969 vs, 1931 s vs, 1906 vs, 1878 s (diethyl ether) |
| | 1991 w m, 1972 vs, 1952 s ($^{13}\text{C}^{18}\text{O}$), 1933 m s, 1905 vs, 1840 m s ($^{13}\text{C}^{18}\text{O}$), 1817 w ($^{13}\text{C}^{18}\text{O}$) (cyclohexane) |
| | 1992 w m, 1970 vs, 1951 s, 1930 s, 1902 vs, 1838 m ($^{13}\text{C}^{18}\text{O}$), 1812 w ($^{13}\text{C}^{18}\text{O}$) (diethyl ether) |

^a Further absorptions of intensities greater than "very weak" (vw) above 650 cm^{-1} : 3115 w, br ($\nu(\text{CH})$); 1424 w, sh ($\omega(\text{C-C})$); 1065 w, 1053 vw w, 1011 w, 1003 w, 996 w, 845 w, 833 vw w, 810 m, 803 m, 791 w m. ^b $^{13}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{18}\text{O}$ enrichment: ca. 20–25 % (calculated from labeled precursor $(\eta^5\text{-C}_5\text{H}_5)\text{Nb}(\text{CO})_{4-n}(\text{*CO})_n$).¹²

Table II. Crystallographically Important Data Collection Information

| | | | |
|---------------------|-----------------------------|--------------------------|--|
| cryst size | 0.15 mm × 0.17 mm × 0.18 mm | | |
| space group | $C_{2h}^2\text{-P2}_1/c$ | $F(000)$ | 1304 |
| a , pm | 1717.0 (8) | nonzero reflections | 3253 |
| b , pm | 775.2 (4) | scanning range | $5.94^\circ \geq 2\theta \geq 4.36^\circ$ |
| c , pm | 1876.0 (8) | molar abs coeff | 15.17 |
| α , deg | 90.0 | μ , cm^{-1} | |
| β , deg | 117.57 (3) | f_{ideal} , cm | 0.131 |
| γ , deg | 90.0 | systematic absences | $0k0$ ($h = 2n + 1$); $h0l$ ($l = 2n + 1$) |
| V , pm^3 | 2213.45×10^6 | | |
| M_r | 670 | | |
| Z | 4 | | |
| d_{obsd} | 2.0 g cm^{-3} | R_{iso} | 0.123 |
| | | R_{aniso} | 0.084 |

ether but largely insoluble in aliphatic hydrocarbons such as pentane. The dark brown solutions are extremely sensitive to air. Great care has thus to be exercised in obtaining spectra from these solutions. It is also advisable to store carefully sealed crystalline samples under an atmosphere of dry nitrogen at -35 °C since some decomposition was experienced when they were left for a few weeks at ordinary temperatures, even in the absence of oxygen.

The same procedure as described for $(\eta^5\text{-C}_5\text{H}_5)_3\text{Nb}_3(\text{CO})_7$ (**4**) was used for the preparation of the labeled derivatives $(\eta^5\text{-C}_5\text{H}_5)_3\text{Nb}_3(\text{*C}^{18}\text{O})_7$ (**5**, ^{13}C); **6**, $^{13}\text{C}^{18}\text{O}$). Both compounds were thus obtained in essentially the same yields (65–85%) and were characterized by means of their IR spectra (Table I) and their field-desorption mass spectra (recording parameters, see above). The purity of **6** was also checked by elemental analysis. Anal. Calcd. for $\text{C}_{22}\text{H}_{15}\text{Nb}_3\text{O}_7$ (670–673, isotopic mixture): C, 39.3; H, 2.3. Found: C, 39.33 (39.40); H, 2.34 (2.48).

X-ray Crystallography

(A) **Data Collection.** A suitable crystal recrystallized from methylene chloride/diethyl ether was glued on a Lindemann capillary which was fastened to a goniometer head. The crystal system, space group, and preliminary unit cell parameters were determined by oscillation and Weissenberg photographs. Exact lattice parameters were calculated by least-squares methods¹⁷ from diffractometrically determined values of 60 selected reflections. Intensity measurements were performed on a com-

(16) W. P. Fehlhammer, W. A. Herrmann, and K. Öfele, in "Handbuch der Präparativen Anorganischen Chemie", 3rd ed., Vol. III, G. Brauer, Ed., Enke Verlag, Stuttgart, West Germany, 1981.

(17) W. Berdesinski and W. Nuber, Neues Jahrb. Mineral. Abh., **104**, 113–146 (1966).

Table III. Positional Parameters ($\times 10^5$ for Nb; $\times 10^4$ for Others) and Thermal Parameters ($\times 10^3$) of $[\eta^5(\mu_3\text{-C}, \mu_2\text{-O})\text{-Carbonyl}]\text{tris}[\text{dicarbonyl}(\eta^5\text{-cyclopentadienyl})\text{niobium}]\text{ (3 Nb-Nb) (4)}^a$

| atom | <i>x/a</i> | <i>y/b</i> | <i>z/c</i> | <i>U</i> ₁₁ | <i>U</i> ₂₂ | <i>U</i> ₃₃ | <i>U</i> ₁₂ | <i>U</i> ₁₃ | <i>U</i> ₂₃ |
|-------|------------|------------|------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| Nb(1) | 12298 (9) | 16481 (16) | 13795 (8) | 65 (1) | 36 (1) | 61 (1) | 3 (1) | 30 (1) | 1 (1) |
| Nb(2) | 26827 (9) | 3901 (16) | 10084 (7) | 61 (1) | 38 (1) | 50 (1) | -2 (1) | 24 (1) | -1 (1) |
| Nb(3) | 29732 (9) | -3651 (20) | 27813 (7) | 58 (1) | 66 (1) | 44 (1) | -8 (1) | 17 (1) | -2 (1) |
| O(11) | 2238 (10) | 5262 (17) | 1681 (10) | 127 (13) | 47 (8) | 159 (15) | -14 (8) | 93 (12) | -9 (9) |
| O(12) | 285 (9) | 2975 (9) | -450 (8) | 100 (11) | 71 (8) | 74 (9) | 7 (8) | 28 (8) | 27 (7) |
| O(21) | 2097 (9) | 3692 (16) | -153 (8) | 108 (11) | 57 (8) | 99 (10) | 10 (8) | 54 (9) | 31 (8) |
| O(22) | 3926 (8) | 3320 (17) | 2172 (8) | 84 (9) | 71 (9) | 92 (10) | -37 (8) | 43 (8) | -27 (8) |
| O(31) | 2773 (11) | 3288 (24) | 3441 (9) | 132 (14) | 115 (14) | 92 (11) | -9 (12) | 50 (11) | -48 (11) |
| O(32) | 1599 (9) | -2260 (22) | 3221 (9) | 93 (11) | 135 (14) | 103 (11) | -5 (10) | 50 (9) | 64 (11) |
| O(33) | 1463 (5) | -832 (11) | 927 (5) | 35 (5) | 37 (5) | 39 (5) | 1 (4) | 7 (4) | 1 (4) |
| C(11) | 1892 (14) | 3919 (23) | 1576 (13) | 103 (16) | 40 (9) | 105 (16) | -4 (10) | 66 (14) | -16 (10) |
| C(12) | 651 (13) | 2477 (22) | 185 (11) | 88 (14) | 42 (9) | 76 (12) | 6 (9) | 37 (11) | 18 (9) |
| C(21) | 2241 (11) | 2493 (21) | 253 (10) | 75 (12) | 47 (9) | 70 (11) | -15 (8) | 40 (10) | 9 (9) |
| C(22) | 3457 (11) | 2251 (21) | 1799 (10) | 66 (11) | 47 (9) | 74 (11) | -7 (11) | 40 (10) | -17 (8) |
| C(31) | 2781 (13) | 1995 (30) | 3127 (12) | 63 (13) | 95 (16) | 73 (13) | 2 (10) | 15 (11) | -27 (12) |
| C(32) | 2048 (11) | -1547 (26) | 3072 (10) | 64 (11) | 86 (13) | 53 (10) | -1 (6) | 25 (9) | 18 (9) |
| C(33) | 2046 (9) | -813 (16) | 1682 (8) | 58 (9) | 31 (7) | 43 (8) | 3 (11) | 27 (7) | 1 (5) |
| C(41) | 550 (14) | 3228 (25) | 2049 (14) | 90 (15) | 62 (12) | 118 (18) | -7 (11) | 78 (15) | -18 (12) |
| C(42) | 705 (12) | 1521 (27) | 2396 (10) | 76 (12) | 85 (13) | 63 (11) | 12 (8) | 49 (10) | -16 (10) |
| C(43) | 210 (10) | 393 (23) | 1771 (11) | 46 (9) | 65 (10) | 90 (13) | 1 (9) | 48 (9) | 8 (10) |
| C(44) | -260 (12) | 1328 (25) | 1037 (11) | 76 (13) | 62 (12) | 80 (13) | 7 (9) | 43 (10) | 2 (9) |
| C(45) | -40 (13) | 3095 (27) | 1235 (14) | 70 (13) | 75 (13) | 109 (17) | 16 (10) | 62 (13) | 12 (12) |
| C(51) | 3481 (13) | -2247 (23) | 1061 (11) | 90 (14) | 55 (10) | 75 (12) | 37 (10) | 45 (11) | 5 (9) |
| C(33) | 2046 (9) | -813 (16) | 1682 (8) | 58 (9) | 31 (7) | 43 (8) | 3 (11) | 27 (7) | 1 (5) |
| C(41) | 550 (14) | 3228 (25) | 2049 (14) | 90 (15) | 62 (12) | 118 (18) | -7 (11) | 78 (15) | -18 (12) |
| C(42) | 705 (12) | 1521 (27) | 2396 (10) | 76 (12) | 85 (13) | 63 (11) | 12 (8) | 49 (10) | -16 (10) |
| C(43) | 210 (10) | 393 (23) | 1771 (11) | 46 (9) | 65 (10) | 90 (13) | 1 (9) | 48 (9) | 8 (10) |
| C(44) | -260 (12) | 1328 (25) | 1037 (11) | 76 (13) | 62 (12) | 80 (13) | 7 (9) | 43 (10) | 2 (9) |
| C(45) | -40 (13) | 3095 (27) | 1235 (14) | 70 (13) | 75 (13) | 109 (17) | 16 (10) | 62 (13) | 12 (12) |
| C(51) | 3481 (13) | -2247 (23) | 1061 (11) | 90 (14) | 55 (10) | 75 (12) | 37 (10) | 45 (11) | 5 (9) |
| C(52) | 2739 (11) | -2106 (19) | 252 (10) | 70 (11) | 40 (8) | 60 (9) | 3 (7) | 31 (9) | -15 (7) |
| C(53) | 2880 (12) | -623 (23) | -82 (9) | 76 (11) | 63 (11) | 55 (9) | 2 (9) | 34 (9) | -10 (8) |
| C(54) | 3663 (12) | 118 (25) | 468 (12) | 70 (12) | 73 (13) | 102 (15) | -13 (10) | 63 (12) | -24 (11) |
| C(55) | 4014 (12) | -830 (25) | 1184 (11) | 78 (13) | 64 (12) | 65 (11) | 7 (9) | 37 (10) | -1 (9) |
| C(61) | 4399 (14) | 319 (41) | 3903 (13) | 56 (13) | 170 (27) | 55 (12) | -29 (16) | -27 (10) | -11 (16) |
| C(62) | 4551 (12) | -468 (37) | 3328 (13) | 54 (12) | 118 (20) | 71 (14) | -2 (13) | 11 (10) | 28 (14) |
| C(63) | 4241 (13) | -2184 (34) | 3185 (11) | 61 (13) | 118 (20) | 54 (11) | 19 (13) | 9 (9) | 19 (12) |
| C(64) | 3889 (12) | -2463 (32) | 3724 (13) | 48 (11) | 101 (17) | 75 (14) | 6 (11) | -1 (10) | 42 (13) |
| C(65) | 3983 (14) | -968 (41) | 4149 (11) | 64 (14) | 142 (24) | 45 (11) | 7 (14) | 4 (10) | 14 (13) |

^a Esd's (given in parentheses) correspond to the least significant digit(s) in this and all other tables throughout this paper.

puter-controlled single-crystal diffractometer (AED Siemens, Mo $K\alpha$ irradiation, θ - 2θ scan technique, five-value method). Reflections less than 2.568 times the standard deviation were not considered. A total of 3253 independent intensities remained for calculation. These were corrected for Lorentz and polarization factors only. Absorption corrections were omitted, the size of the crystal used for intensity measurement being smaller than the optimum thickness ($t_{\text{opt}} = 0.131$ cm). The crystal data are listed in Table II.

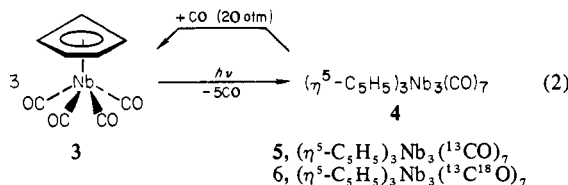
(B) **Structure Analysis and Refinement.** The monoclinic species ($C_{2h}^2-P2_1/c$) contains four molecules per unit cell. Thus $(\eta^5\text{-C}_5\text{H}_5)_3\text{Nb}_3(\text{CO})_7$ comprises the asymmetric unit cell. The structure was solved by three-dimensional Patterson and Fourier syntheses. Refinement with isotropic and anisotropic temperature factors resulted in $R = 0.123$ and $R_w = 0.084$, respectively. We were not able to locate the hydrogen atoms, either by a difference Fourier map or by the help of a model. The atomic coordinates are listed in Table III and bond lengths and other molecule parameters in Table IV.

All calculations were performed on computers Siemens 301 (Anorganisch-chemisches Institut, Heidelberg) and IBM 370/168 (Computer Center, Universität Heidelberg) with local versions of the X-ray 70 system.¹⁸ Scattering factors were those of Hanson, Herman, Lea, and Skillman.¹⁹ The numbering scheme corresponds to those in the figures. The thermal parameters take the form $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ with $\beta_{ij} = 2\pi^2 U_{ij} a_i^* a_j^*$.

Results and Discussion

(A) **Synthesis and Spectroscopy.** The observation that a polynuclear carbonylniobium compound is formed from tetracarbonyl(η^5 -cyclopentadienyl)niobium (3) was initially made

during a systematic investigation of the high-pressure carbonylation of dichlorobis(η^5 -cyclopentadienyl)niobium, $(\eta^5\text{-C}_5\text{H}_5)_2\text{NbCl}_2$,¹¹ when solutions of $(\eta^5\text{-C}_5\text{H}_5)\text{Nb}(\text{CO})_4$ (3) in hexane were prepared for the purpose of recrystallization of the crude product resulting from the above-mentioned reaction after column chromatography, variable amounts of a brown fluffy powder separated from these solutions even under scrupulous exclusion of air and moisture. Diffuse daylight was very quickly recognized to induce partial elimination of carbon monoxide from the "half-sandwich" complex 3, accompanied by cluster formation the coordinatively unsaturated metal-carbonyl fragments generated by this means¹¹ (eq 2).



Keeping in mind that the cheapest, cleanest and most productive method of preparing enneacarbonyldiiron, $\text{Fe}_2(\text{CO})_9$, is still the original one as described by Speyer, who employed sunlight in order to induce carbonyl elimination from $\text{Fe}(\text{CO})_5$,^{20,21} we expected this old-fashioned outdoor method would also hold promise for yielding crystalline 4 right away. In fact, exposure of hexane solutions of $(\eta^5\text{-C}_5\text{H}_5)\text{Nb}(\text{CO})_4$ (3) to more or less bright sunlight

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Table IV. Molecular Parameters of $[\eta^2(\mu_3\text{-C}, \mu_2\text{-O})\text{-Carbonyl}] \text{tris}[\text{dicarbonyl}(\eta^5\text{-cyclopentadienyl})\text{niobium}](3 \text{ Nb-Nb})$ (4)^a

| A. Bond Lengths (pm) | | | | C. Bond Angles (deg) | | | | | |
|---|------------|---|-------------------------|---|-----------|-------------------|------------|-------|-------|
| Nb(1)-Nb(2) | 304.4 (2) | C(11)-O(11) | 116.9 (23) | Nb(1)-Nb(2)-Nb(3) | 64.43 (5) | Nb(2)-Nb(3)-C(33) | 43.8 (5) | | |
| Nb(1)-Nb(3) | 332.0 (2) | C(12)-O(12) | 112.8 (22) | Nb(2)-Nb(1)-Nb(3) | 59.79 (5) | Nb(2)-Nb(3)-O(33) | 40.7 (2) | | |
| Nb(2)-Nb(3) | 318.1 (2) | C(21)-O(21) | 115.5 (22) | Nb(1)-Nb(3)-Nb(2) | 55.79 (4) | Nb(1)-C(33)-Nb(2) | 85.0 (4) | | |
| Nb(1)-O(33) | 221.2 (10) | C(22)-O(22) | 114.2 (20) | Nb(2)-Nb(1)-C(11) | 82.5 (7) | Nb(1)-C(33)-Nb(3) | 102.7 (6) | | |
| Nb(1)-C(11) | 203.6 (19) | C(31)-O(31) | 116.6 (30) | Nb(2)-Nb(1)-C(12) | 83.5 (7) | Nb(2)-C(33)-Nb(3) | 98.5 (7) | | |
| Nb(1)-C(12) | 208.8 (19) | C(32)-O(32) | 108.2 (29) | Nb(2)-Nb(1)-C(33) | 46.8 (5) | Nb(1)-O(33)-Nb(2) | 86.3 (3) | | |
| Nb(1)-C(33) | 227.8 (14) | C(33)-O(33) | 130.3 (14) | Nb(2)-Nb(1)-O(33) | 47.2 (3) | Nb(1)-O(33)-Nb(3) | 71.9 (2) | | |
| Nb(1)-C(41) | 240.9 (29) | C(41)-C(42) | 144.2 (30) | Nb(3)-Nb(1)-C(11) | 92.2 (5) | Nb(2)-O(33)-Nb(3) | 67.9 (2) | | |
| Nb(1)-C(42) | 245.9 (25) | C(42)-C(43) | 139.1 (25) | Nb(3)-Nb(1)-C(12) | 143.2 (6) | C(42)-C(41)-C(45) | 108.5 (17) | | |
| Nb(1)-C(43) | 239.6 (22) | C(43)-C(44) | 143.0 (26) | Nb(3)-Nb(1)-C(33) | 35.3 (3) | C(41)-C(42)-C(43) | 106.5 (16) | | |
| Nb(1)-C(44) | 234.4 (22) | C(44)-C(45) | 142.5 (29) | Nb(3)-Nb(1)-O(33) | 68.8 (2) | C(42)-C(43)-C(44) | 110.1 (17) | | |
| Nb(1)-C(45) | 235.5 (24) | C(45)-C(41) | 139.1 (30) | Nb(1)-Nb(2)-C(21) | 79.9 (6) | C(43)-C(44)-C(45) | 106.0 (16) | | |
| Nb(2)-O(33) | 223.8 (10) | C(51)-C(52) | 144.3 (27) | Nb(1)-Nb(2)-C(22) | 86.2 (6) | C(41)-C(45)-C(44) | 108.9 (18) | | |
| Nb(2)-C(21) | 206.1 (16) | C(52)-C(53) | 138.5 (22) | Nb(1)-Nb(2)-C(33) | 48.2 (4) | C(52)-C(51)-C(55) | 108.0 (16) | | |
| Nb(2)-C(22) | 205.6 (15) | C(53)-C(54) | 138.4 (24) | Nb(1)-Nb(2)-O(33) | 46.5 (3) | C(51)-C(52)-C(53) | 106.2 (14) | | |
| Nb(2)-C(33) | 222.6 (18) | C(54)-C(55) | 140.0 (28) | Nb(3)-Nb(2)-C(21) | 134.0 (6) | C(52)-C(53)-C(54) | 108.6 (15) | | |
| Nb(2)-C(51) | 243.7 (20) | C(55)-C(51) | 137.9 (29) | Nb(3)-Nb(2)-C(22) | 68.8 (6) | C(53)-C(54)-C(55) | 109.7 (19) | | |
| Nb(2)-C(52) | 242.6 (18) | C(61)-C(62) | 136.6 (41) | Nb(3)-Nb(2)-C(33) | 37.7 (3) | C(51)-C(55)-C(54) | 107.2 (15) | | |
| Nb(2)-C(53) | 235.8 (22) | C(62)-C(63) | 141.0 (38) | Nb(3)-Nb(2)-O(33) | 71.5 (2) | C(62)-C(61)-C(65) | 104.4 (26) | | |
| Nb(2)-C(54) | 234.2 (27) | C(63)-C(64) | 141.4 (39) | Nb(1)-Nb(3)-C(31) | 66.9 (5) | C(61)-C(62)-C(63) | 112.3 (26) | | |
| Nb(2)-C(55) | 235.2 (22) | C(64)-C(65) | 137.1 (39) | Nb(1)-Nb(3)-C(32) | 84.1 (4) | C(62)-C(63)-C(64) | 105.0 (23) | | |
| Nb(3)-C(31) | 202.0 (24) | C(65)-C(61) | 142.7 (43) | Nb(1)-Nb(3)-C(33) | 42.0 (4) | C(63)-C(64)-C(65) | 108.1 (23) | | |
| Nb(3)-C(32) | 211.7 (23) | Nb(1)-C ₅ H ₅ (centr) | 206.4 (5) ^b | Nb(1)-Nb(3)-O(33) | 39.3 (2) | C(61)-C(65)-C(64) | 110.2 (25) | | |
| Nb(3)-C(33) | 196.6 (12) | Nb(2)-C ₅ H ₅ (centr) | 206.0 (13) ^b | Nb(2)-Nb(3)-C(31) | 101.5 (7) | Nb(3)-C(33)-O(33) | 169.6 (11) | | |
| Nb(3)-C(61) | 243.9 (19) | Nb(3)-C ₅ H ₅ (centr) | 208.9 (3) ^b | Nb(2)-Nb(3)-C(32) | 125.2 (4) | Nb(1)-C(11)-O(11) | 177 (2) | | |
| Nb(3)-C(62) | 241.4 (21) | | | C(11)-Nb(1)-C(12) | 82.9 (8) | Nb(1)-C(12)-O(12) | 174 (2) | | |
| Nb(3)-C(63) | 240.4 (24) | | | C(21)-Nb(2)-C(22) | 81.4 (6) | Nb(2)-C(21)-O(21) | 174 (2) | | |
| Nb(3)-C(64) | 238.1 (22) | | | C(31)-Nb(3)-C(32) | 93.1 (9) | Nb(2)-C(22)-O(22) | 175 (2) | | |
| Nb(3)-C(65) | 238.4 (18) | | | | | Nb(3)-C(31)-O(31) | 174 (2) | | |
| | | | | | | Nb(3)-C(32)-O(32) | 175 (2) | | |
| B. Selected Nonbonding Contact Distances (pm) | | | | D. Selected Molecular Planes ^c | | | | | |
| Nb(1)···C(21) | 336.2 (24) | Nb(3)···O(33) | 325.6 (7) | plane I | C(41) | C(42) | C(43) | C(44) | C(45) |
| Nb(1)···C(31) | 313.6 (17) | Nb(3)···C(22) | 310.0 (20) | dev, pm | 0.62 | -0.35 | -0.03 | 0.41 | -0.65 |
| Nb(1)···C(32) | 317.4 (19) | | | plane II | C(51) | C(52) | C(53) | C(54) | C(55) |
| | | | | dev, pm | 1.68 | -0.34 | -1.11 | 2.18 | -2.40 |
| | | | | plane III | C(61) | C(62) | C(63) | C(64) | C(65) |
| | | | | dev, pm | -0.22 | 0.40 | -0.42 | 0.30 | -0.05 |

^a Standard deviations given in parentheses correspond to the last digit(s) in this and other tables throughout this paper. ^b Corresponds to the calculated distances between respective niobium atoms and the best planes defined by the respective C₅H₅ rings (see section D of this table). ^c The interplanar angle Nb(1), Nb(2), Nb(3) vs. Nb(3), C(33), O(33) amounts to 84.9°.

proved an immediate, effective way for the synthesis of *crystalline* products if care is taken that these solutions are allowed to stand without agitation at +18.0 °C (see section 1 in Experimental Section). The yields of *crystalline*, analytically pure product range between 65 and 82%, with the reaction period strongly depending upon the light intensity, of course.

Compound 4 forms black lustrous, nonsublimable needles (from hexane) or big shining cubes (from methylene chloride/diethyl ether) which can be handled in air for a brief period of time. Prolonged exposure to air, however, is accompanied by gradual deterioration of even crystalline samples; $(\eta^5\text{-C}_5\text{H}_5)\text{Nb}(\text{CO})_4$ is formed among intractable materials upon decomposition. That the formula $(\eta^5\text{-C}_5\text{H}_5)_3\text{Nb}_3(\text{CO})_7$ represents the correct composition of 4 was established by means of elemental analyses and field-desorption mass spectrometry, the latter giving the parent ion peak at m/e 670 (acetone); no additional fragments are observed.

¹H and ¹³C NMR as well as IR spectroscopy revealed an unsymmetric molecule: the three cyclopentadienyl groups show up with two distinct, sharp singlets, displaying an intensity ratio of exactly 1:2, at τ 4.34 and 4.48, respectively, in the ¹H NMR spectra (acetone-*d*₆, +33 °C, internal Me₄Si). This finding unequivocally proves the presence of two chemically and magnetically different sets of cyclopentadienyl protons. The same statement adequately holds for the general feature of the ¹³C NMR spectra: again, two instead of just one signals are observed at δ 95.26 and 94.40, respectively, for a total of 15 ring carbons (CD₂Cl₂, +34 °C, internal Me₄Si). The seven carbonyl ligands are represented by a fairly broad adsorption ($\Delta\nu_{1/2} \approx 150$ Hz) centered around 247 ppm ($\delta(\text{CO})$; ca. 20% ¹³CO enrichment). Since nuclei directly attached to niobium (⁹³Nb; spin 9/2, 100%) experience quadrupol

broadening (which is especially true for the carbonyl carbons), ¹³C NMR spectroscopy fails to provide a means of tracing fluxional processes in organometallic niobium complexes. In hopes of achieving information on the dynamic behavior of this particular compound, ⁹³Nb NMR spectra were recorded as well: the ⁹³Nb NMR results on $(\eta^5\text{-C}_5\text{H}_5)_3\text{Nb}_3(\text{CO})_7$ (4)²² are presented graphically in Figure 1. For comparison, data on $(\eta^5\text{-C}_5\text{H}_5)\text{Nb}(\text{CO})_4$ (3), which is characterized by a narrow NMR signal, are included. 3 is increasingly formed as a decomposition product of the trimeric cluster in solution and can be detected by NMR spectroscopy in a freshly prepared THF solution of the niobium cluster after ca. 30 min (300 K). At elevated temperatures, decomposition occurs more rapidly. A THF solution allowed to stand at 340 K for 2 h contains approximately 20% of the niobium species in the form of $(\eta^5\text{-C}_5\text{H}_5)\text{Nb}(\text{CO})_4$.

In addition to the apparent dependence of the chemical shift values $\delta(^{93}\text{Nb})$ on the temperature, there is a slight dependence upon the solvent: $(\eta^5\text{-C}_5\text{H}_5)\text{Nb}(\text{CO})_4/\text{THF}$, -2047 (210 K) to -1998 (340 K) ppm (temperature gradient 0.38 ppm/deg); $(\eta^5\text{-C}_5\text{H}_5)\text{Nb}(\text{CO})_4/\text{CH}_2\text{Cl}_2$: -2028 (240 K) to -2005 (300 K) ppm (temperature gradient 0.42 ppm/deg); $(\eta^5\text{-C}_5\text{H}_5)_3\text{Nb}_3(\text{CO})_7/\text{CH}_2\text{Cl}_2$ at 295 K: $\delta(^{93}\text{Nb})$ -1762 ± 5, line width $\Delta\nu_{1/2} = 2900 \pm 480$ Hz.

The consistent decrease of shielding σ (decrease of $|\delta(^{93}\text{Nb})|$) with increasing temperature for $(\eta^5\text{-C}_5\text{H}_5)\text{Nb}(\text{CO})_4$ is in accord with an expected increase of the paramagnetic contribution σ_{para}

(22) The ⁹³Nb NMR spectra were taken from saturated solutions of 4 at 22.00 MHz on a Bruker WH-90 spectrometer using NbCl₅/CH₃CN as external standard ($\delta(\text{Nb})$ 0; lock, external acetone-*d*₆; ca. 2000 scans per spectrum; negative values; high-field of NbCl₅).

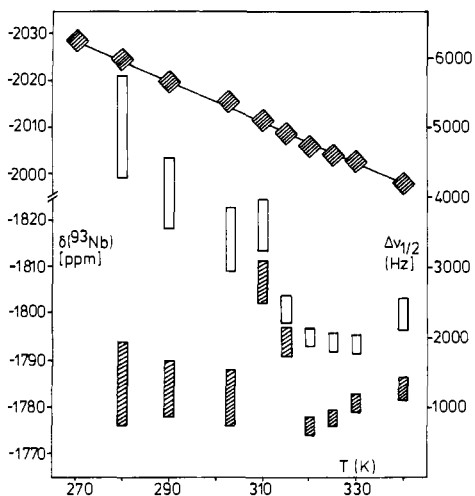


Figure 1. Temperature vs. ^{93}Nb chemical shift $\delta(^{93}\text{Nb})$ (relative to $\text{NbCl}_5/\text{CH}_3\text{CN}$; left ordinate and shaded symbols) and half-widths $\Delta\nu_{1/2}$ (right ordinate and open symbols) for $(\eta^5\text{-C}_5\text{H}_5)_3\text{Nb}_3(\text{CO})_7$, 0.15 M in THF. The vertical length and horizontal width of the bars indicate the absolute error as obtained from an iterative Newton fit. The upper line shows $\delta(^{93}\text{Nb})$ values for $(\eta^5\text{-C}_5\text{H}_5)\text{Nb}(\text{CO})_4/\text{THF}$. The $\Delta\nu_{1/2}$ values for this compound are around 20 Hz. The spectra (22.0 MHz) were obtained on a Bruker WH 90 PFT spectrometer in 7.5-mm diameter vials at a sweep width of 31.25 kHz and a pulse width of 5 μs (no repetition time). The average number of scans was 2000.

to the overall shielding $\sigma = \sigma_{\text{dia}} + \sigma_{\text{para}}$. The σ_{para} term, which is mainly determined by the excitation energy for electronic transitions ($\sigma_{\text{para}} \propto \Delta E^{-1}$),²³ becomes larger as the population of vibronic levels increases with increasing temperature.²⁴ Accordingly, σ decreases, as shown with the "normal" behavior of $(\eta^5\text{-C}_5\text{H}_5)\text{Nb}(\text{CO})_4$. This temperature effect is commonly observed in metal NMR spectroscopy.²⁵

$|\delta(^{93}\text{Nb})|$ values of **4** are approximately 200 ppm below those of the parent compound **3**; i.e. the ^{93}Nb nucleus is shielded to a lower extent in the cluster than in the monomeric species, which fact is not unexpected, since the former exhibits a lower point symmetry (C_s at the best for an isolated $[(\eta^5\text{-C}_5\text{H}_5)\text{Nb}(\text{CO})_2]$ moiety). Due to the low symmetry, the electric field gradient tensor at the ^{93}Nb nuclei becomes fully effective ($I(^{93}\text{Nb}) = 9/2$), thus increasing quadrupolar relaxation which, together with scalar interaction between the ^{93}Nb nuclei and possibly dynamic contributions, accounts for the large half-width of the ^{93}Nb NMR signals, mainly at temperatures below 315 K.

In contrast to $(\eta^5\text{-C}_5\text{H}_5)\text{Nb}(\text{CO})_4$, $\delta(^{93}\text{Nb})$ values for the trimeric cluster exhibit an "abnormal" behavior above 303 K inasmuch as there is a maximum shielding at 310 ± 1 K ($\delta(^{93}\text{Nb}) = -1807.2 \pm 4.4$) and a slight increase in going from 320 to 340 K. This trend is paralleled by similar variations of the line width. A line shape analysis also reveals that, for the absorptions appearing between 310 and 330 K, the signals are only 20% Lorentzian (while the Lorentzian component is ca. $90 \pm 20\%$ for the signals below 310 and above 330 K). These facts, while they do not allow a detailed description of the dynamic behavior of **4**, show a dynamic component contributing to the shielding of the ^{93}Nb nucleus at temperatures above 303 K, which could be provided either by fluxional processes within the molecule or by intermolecular exchange equilibria. Similar temperature effects have previously been observed in the ^{51}V NMR spectra of vanadyl esters.²⁶ In the light of a recent ^1H NMR study of $(\eta^5\text{-$

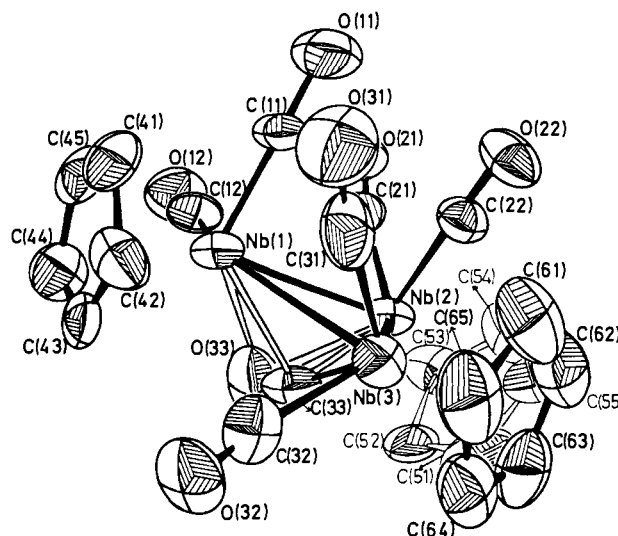


Figure 2. The molecular structure of $[\eta^2(\mu_3\text{-C}, \mu_2\text{-O})\text{-carbonyl}]\text{tris}[\text{di-carbonyl}(\eta^5\text{-cyclopentadienyl})\text{niobium}] (3\text{Nb-Nb})$ (**4**). The vibrational ellipsoids are drawn at 50% probability level.

$\text{C}_5\text{H}_4\text{CH}_3)_3\text{Nb}_3(\text{CO})_7$,²⁷ time averaging of the niobium nuclei is best interpreted as an outcome of fluxional behavior of at least the bridging carbonyl.

The IR spectra resemble well-refined multiband patterns in the area which covers the CO stretching vibrations (compare Table I). Once again, no definite conclusion can be drawn from the observed spectra in regards to the metal-carbonyl fragments in **4**. A notable feature of the solid-state IR spectra is a sharp absorption of medium intensity at 1330 cm^{-1} . We have never observed a band in this region in any niobium compound which structurally is based upon $(\eta^5\text{-C}_5\text{H}_5)\text{Nb}(\text{CO})_x$ fragments, nor is there an absorption present in the parent compound $(\eta^5\text{-C}_5\text{H}_5)\text{-Nb}(\text{CO})_4$ itself.^{11,12} ^{13}C - as well as $^{13}\text{C}^{18}\text{O}$ -labeling experiments clearly assign this absorption to a carbonyl ligand which ought to be coordinated in some strange fashion (eq 2 and Table I). By way of contrast, no absorptions in the 1300-cm^{-1} area appear in the solution IR spectra listed in Table I. Two explanations must be considered to account for this difference between the solid state and the solution infrared spectra: (i) the molecule does not maintain its solid-state geometry (see below) upon dissolution or (ii) the intensity of the corresponding vibration is exceedingly low.

The trinuclear niobium complex **4** exhibits a notable tendency of declusterification upon carbonylation: the parent carbonyl $(\eta^5\text{-C}_5\text{H}_5)\text{Nb}(\text{CO})_4$ (**3**) is formed in quantitative yield after a solution of **4** in THF has been treated with carbon monoxide (20 atm) at room temperature for a period of 10 h (eq 2). This clean of a CO-induced degradation reaction is actually not common for the majority of polynuclear metal carbonyls and further supports the idea that the kind of semibringing carbonyl discussed in the following section enhances their reactivity.

(B) Molecular Structure: The $\eta^2(\mu_3\text{-C}, \mu_2\text{-O})$ Bonding of Carbon Monoxide. Since the ^1H , ^{13}C , and ^{93}Nb NMR spectra as well as the IR data did not permit unambiguous structural assignment, we have carried out a single-crystal X-ray structure determination. The niobium cluster **4** crystallizes from methylene chloride/ether (1:1) in the monoclinic space group $C_{2h}^2-P2_1/c$. Further crystallographic data are given in Table II. Positional and thermal parameters are listed in Table III. Bond lengths and bond angles are compiled in Table IV. The molecular structure of $(\eta^5\text{-C}_5\text{H}_5)_3\text{Nb}_3(\text{CO})_7$ has the following characteristics worthy of being discussed in greater detail.

(1) The Metal Framework. As depicted in Figures 2–4, the trinuclear molecule centers around a triangular frame defined by the niobium atoms which arises from aggregation of the photochemically generated $(\eta^5\text{-C}_5\text{H}_5)\text{Nb}(\text{CO})_x$ fragments ($x = 2$ and 3, respectively). The metal-metal separations ranging between

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Table V. Comparison of Structural Characteristics of Some Closely Related Niobium Complexes

| compd | $d(\text{Nb-Nb})$, pm | $d(\text{Nb-C,CO})^a$, pm | $d(\text{C-O})^a$, pm | ref |
|--|------------------------|----------------------------|-------------------------|-----------|
| $(\eta^5\text{-C}_5\text{H}_5)_3\text{Nb}_3(\text{CO})_7$ | 304.4 (2) | 208.8 (19) | 112.8 (22) | this work |
| | 318.1 (2) | 203.6 (19) | 116.9 (23) | |
| | 332.0 (2) | 206.1 (16) | 115.5 (22) | |
| | | 205.6 (15) | 114.2 (20) | |
| | | 202.0 (24) | 116.6 (30) | |
| | | 211.7 (23) | 108.2 (29) | |
| | | 196.6 (12) ^b | 130.3 (14) ^b | |
| $(\eta^5\text{-C}_5\text{H}_5)\text{Nb}(\text{CO})_4$ | | 208.1 (7) | 111.8 (11) | 30 |
| $(\eta^5\text{-C}_5\text{H}_5)_3\text{Nb}_2(\text{CO})_4(\mu\text{-H})$ | 373.8 (3) | 210.3 (8) | 114.0 (9) | 13, 14 |
| | | 205.1 (18) | 116.4 (24) | |
| | | 204.7 (18) | 116.5 (22) | |
| | | 205.5 (14) | 117.5 (16) | |
| $(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})\text{Nb}(\mu\text{-CO})\text{Co}(\text{CO})_3$ | 299.2 (1) ^c | 201.6 (14) | 118.6 (17) | 32 |
| | | 205.8 (4) | 114.0 (4) | |
| | | 253.1 (4) ^b | 116.5 (4) ^b | |
| $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{Nb}(\mu\text{-H})\text{Fe}(\text{CO})_4$ | 332.4 (1) ^d | 205.7 (4) | 115.0 (5) | 33 |
| $(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb}_2(\mu\text{-H})_2(\mu\text{-C}_5\text{H}_4)_2$ | 310.5 (6) | | | 29 |

^a Entries placed in the same line correspond to the same carbonyl ligand. ^b Semibridging carbonyl. ^c Nb-Co separation. ^d Nb-Fe separation.

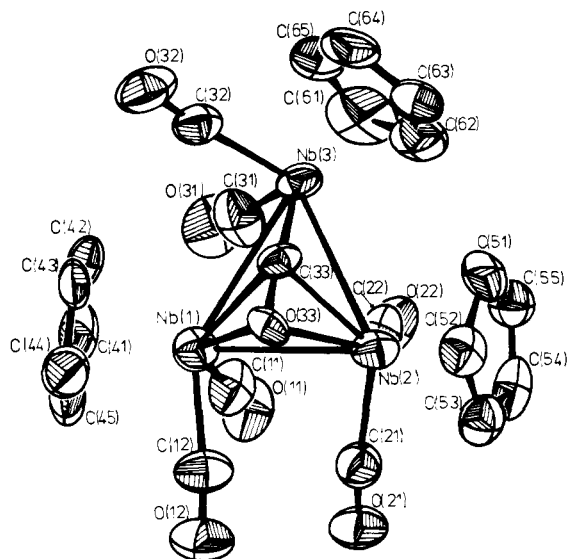


Figure 3. ORTEP view of 4 from the top of the triply semibridging carbonyl ligand (50% probability thermal ellipsoids). The representation shows that the molecule has no element of symmetry.

304 and 332 pm exceed the theoretical value of 294 pm calculated from the corresponding metallic radius.²⁸ On the other hand, these distances very well compare to the Nb-Nb bond length of 310.5 (6) pm in the niobocene dimer of composition $(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb}_2(\mu\text{-H})_2(\mu\text{-C}_5\text{H}_4)_2$,²⁹ beyond that, they are far shorter than the metal-metal separations (373.8 (3) and 345.3 (2) pm, respectively) found in the related μ -hydrido complexes $(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb}(\text{CO})\text{-H-Nb}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)$ and $(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb}(\text{CO})\text{-H-Cr}(\text{CO})_5$,^{13,14,30} When the fact that the covalent radii of molybdenum and cobalt are slightly smaller than that of niobium is taken into account,²⁸ reasonable comparison might also be made with the intermetallic distances in the heterodinuclear carbonyl complexes $(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb}(\mu\text{-CO})_2\text{Mo}(\text{CO})(\eta^5\text{-C}_5\text{H}_5)$ (307.3 (1) pm),³¹ $(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})\text{Nb}(\mu\text{-CO})\text{Co}(\text{CO})_3$ (299.2 (1) pm),³² and $(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})\text{Nb}(\mu\text{-H})\text{Fe}(\text{CO})_4$ (332.4 (1) pm).^{33,34}

(28) A. F. Wells, "Structural Inorganic Chemistry", 3rd ed., Clarendon Press, Oxford, England, 1962.

(29) L. J. Guggenberger, *Inorg. Chem.*, **12**, 294 (1973).

(30) M. L. Ziegler, P. Wülknitz, H. Biersack, and W. A. Herrmann, unpublished results. Note that hydrido bridges are well-known to significantly lengthen the corresponding metal-metal bond; cf. H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, **72**, 231 (1972), and literature cited therein.

(31) A. A. Pasyanski, Yu. V. Skripkin, I. L. Eremenko, V. T. Kalinnikov, G. G. Aleksandrov, V. G. Andrianov, and Yu. T. Struchkov, *J. Organomet. Chem.*, **165**, 49 (1979).

(32) K. S. Wong, W. R. Scheidt, and J. A. Labinger, *Inorg. Chem.*, **18**, 1709 (1979).

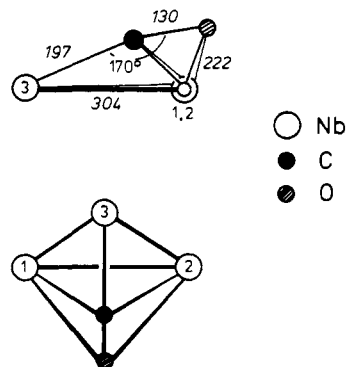


Figure 4. Sketches of the $\text{Nb}_3(\eta^2\text{-CO})$ backbone along the $\text{Nb}(1)\text{-Nb}(2)$ vector (upper) and down the $\text{O-C-Nb}(3)$ plane (lower). Note that the drawings are not true to scale.

(2) **The Ligands.** Each of the niobium atoms bears a symmetrically π -bonded cyclopentadienyl group, the interatomic distances and angles of which very much resemble those of other related carbonylniobium compounds listed in Table V.^{13,30-33} The arrangement of the C_5H_5 ligands is such that the resulting $(\eta^5\text{-C}_5\text{H}_5)_3\text{Nb}_3$ skeleton lacks any element of symmetry (Figures 2, 3, and 5).

Six out of seven carbonyl ligands present in the molecule are coordinated in an essentially linear, conventional terminal fashion and compare well with the parameters of the parent compound $(\eta^5\text{-C}_5\text{H}_5)\text{Nb}(\text{CO})_4$.³⁵ Unprecedented to date, however, are the structural characteristics of the seventh carbonyl group: although terminally bonded to the metal center $\text{Nb}(3)$, thus representing an almost linear metal-carbonyl functionality, its close contact with the remaining metal atoms $\text{Nb}(1)$ and $\text{Nb}(2)$ documents true bonding interactions. The corresponding distances (Table V) are admittedly 24–30 pm greater than the $\text{Nb}(3)\text{-C}(33)$ separation (196.6 (12) pm), responsible for terminal coordination, but only

(33) K. S. Wong, W. R. Scheidt, and J. A. Labinger, *Inorg. Chem.*, **18**, 136 (1979).

(34) It would be very bold, however, to draw any conclusion regarding the metal-metal bond orders of 4 from the observed bond lengths: first, there is not yet enough data available on organometallic niobium compounds containing metal-to-metal interactions which are bonding in nature. Second, great care has to be exercised in correlating bond orders vs. bond distances; the latter aspect was emphasized by Bernal et al., who have shown that in some cases bond orders between two adjacent metals are not correlatable with bond lengths and vice versa; cf. I. Bernal, J. D. Korp, M. G. Reisner, and W. A. Herrmann, *J. Organomet. Chem.*, **139**, 321 (1977); I. Bernal, M. Creswick, and W. A. Herrmann, *Z. Naturforsch., B: Anorg. Chem. Org. Chem.*, **34B**, 1345 (1979).

(35) I. Bernal et al., unpublished results, 1979. We thank Professor Bernal (Houston, TX) for his permission to quote these data prior to publication; see also: W. A. Herrmann, W. Kalcher, H. Biersack, M. Creswick, and I. Bernal, *Chem. Ber.*, in press.

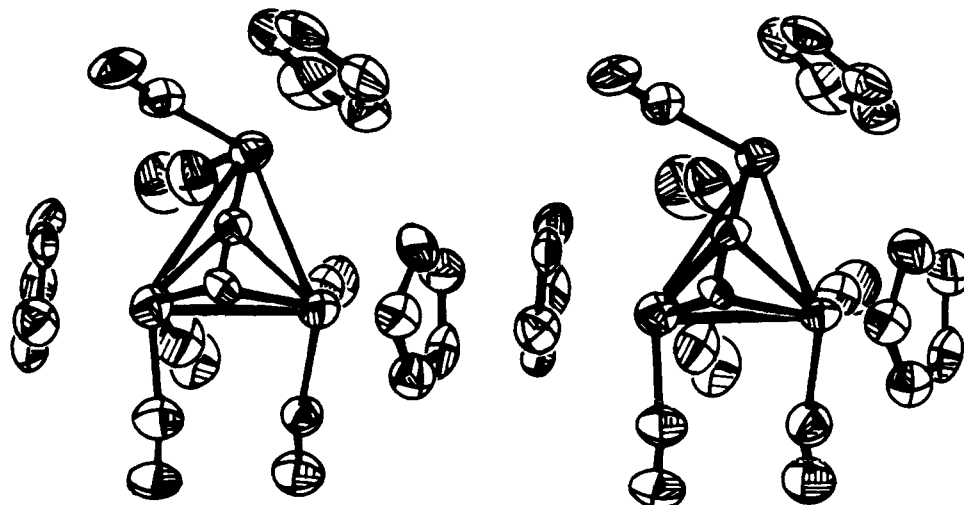
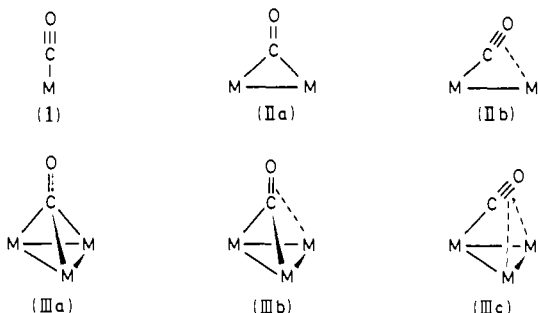


Figure 5. Stereoview of the niobium cluster 4. Thermal ellipsoids again correspond to 50% probability.

slightly longer than the sum of the covalent Pauling radii (cf. Table V). Apart from one exception,³⁶ M...CO distances on the order of 230–250 pm have hitherto been reported for “semibridging” systems of types IIb and IIIb (M = V,⁹ Mo,³⁷ Rh,³⁸ Co/Nb,³¹ Fe,³⁹ Pt,⁴⁰ etc.) whereas the M–CO distances are close to 190 pm.⁴¹ The plane defined by Nb(3), C(33), and O(33) is practically perpendicular to the Nb₃ skeleton, with the intersecting line hardly deviating from the bisector which passes through Nb(3).



Apart from a vast number of terminal (I), edge-bridging (IIa), and face (or triply)-bridging (IIIa) carbonyls which comprise the classical bonding types of metal-attached carbon monoxide,⁴² CO bridges in which the π system of the carbonyl unit engages in bonding interaction with a further metal center have recently been discovered. For the latter, the designation semibridging⁴³ has been

(36) C. J. Commons and B. F. Hoskins, *Aust. J. Chem.*, **28**, 1663 (1975). In this paper, a semibridging Mn–CO distance of 201 (3) pm associated with a carbonyl bond length of 110 (4) pm has been reported for Mn₂(CO)₄(μ -CO)(μ -dpm)₂. The corresponding Mn–O separation amounts to 229 (2) pm.

(37) R. J. Klingler, W. M. Butler, and M. D. Curtis, *J. Am. Chem. Soc.*, **100**, 5034 (1978).

(38) W. D. Jones, M. A. White, and R. G. Bergman, *J. Am. Chem. Soc.*, **100**, 6770 (1978).

(39) M. Manassero, M. Sansoni, and G. Longoni, *J. Chem. Soc., Chem. Commun.*, 919 (1976). The tetranuclear anion [Fe₄(CO)₁₃H][−] structurally described in this paper, gives an example of semi-triply bridging carbonyl functionalities (M₂ > C=O–M). The iron–oxygen distance is amazingly short in this case (200 pm; d(C–O) = 126 pm, ν (CO) = 1645 cm^{−1}).

(40) P. M. Brown, R. J. Puddephatt, M. Rashidi, Lj. Manojlović-Muir, K. W. Muir, T. Solomun, and K. R. Seddon, *Inorg. Chim. Acta*, **23**, L33 (1977); M. P. Brown, A. N. Keith, Lj. Manojlović-Muir, K. W. Muir, R. J. Puddephatt, and K. R. Seddon, *ibid.*, **34**, L233 (1979).

(41) For a comprehensive review on symmetrically bridging, asymmetrically bridging, and semibridging carbon monoxide complexes, see: R. Colton and M. J. McCormick, *Coord. Chem. Rev.*, **31**, 1 (1980), and the literature cited therein.

(42) The term “classical” may not be misunderstood in terms of historically old, however. We therefore wish to draw the reader’s attention to the fact that the very first example of IIIa was Fischer’s (η^5 -C₅H₅)₃Ni₃(CO)₂ which was prepared as late as in 1958 and structurally characterized by Mills et al. in 1961 (E. O. Fischer and C. Palm, *Chem. Ber.*, **91**, 1725 (1958); A. A. Hock and O. S. Mills in “The Chemistry of Coordination Compounds”, S. Kirshner, Ed., Macmillan, New York, p 640.

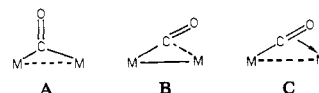
proposed⁸ and widely used. As a counterpart (or better, variant) of IIa, type IIb frameworks are characteristic, for example, of (η^5 -C₅H₅)₂V₂(CO)₅^{8,9} and (η^5 -C₅H₅)₂Mo₂(CO)₄,³⁷ whereas the η^2 (μ_3 -C) arrangement IIIb describes the salient structural element of Bergman’s trinuclear anion [(η^5 -C₅H₅)₂Rh₃(CO)₄][−],³⁸ with [Fe₄(CO)₁₃H][−] being a borderline case between those two extremes.^{39,44} The niobium trimer (η^5 -C₅H₅)₃Nb₃(CO)₇ extends the triple bridge series inasmuch as the unique CO ligand edge bridges via the carbon; the descriptor thus takes the form η^2 (μ_3 -C, μ_2 -O).^{45,46}

As a consequence of this additional twofold bridging function, the C(33)–O(33) separation is thus dramatically lengthened (130.3 (14) pm) as compared to normal (Nb–)C–O distances which cover the range between 108 and 119 pm (Table V). In keeping with the requirements of the synergetic mechanism of bonding of carbon monoxide to transition metals, the Nb(3)–C(33) bond length (196.6 (12) pm) is markedly shorter than those of the other, exclusively terminally bonded carbonyl groups (202–212 pm; cf. Table V).

(3) η^2 (μ_3 -C, μ_2 -O) Complexation. An Attempt at Explanation of the Formal Six-Electron Ligand. In our opinion, semi-triply bridging becomes understandable in the present case on considering the electronic requirements of the (η^5 -C₅H₅)Nb(CO)_x units (x = 2 and 3): Nb(3) which bears one cyclopentadienyl ring and three CO’s has an 18-electron configuration and thus meets the EAN rule. By way of contrast, Nb(1) and Nb(2) have one CO ligand less each; these (η^5 -C₅H₅)Nb(CO)₂ fragments represent 16-electron species calling for stabilization which is in fact provided by the sterically available CO group formally belonging to the Nb(3) center. This unique ligand now acts as a donor bridge and thus alleviates the electronically unsaturated situation at the other niobium centers. Neutralization of unequal charge distribution

(43) This terminology is also used in the German literature, since a word-by-word translation would yield “halbverbrückt” which is misleading to the extent that it gives a wrong impression of the substantial content. We therefore suggest to either not translate “semibridging” or instead use the term “quasi-verbrückte Carbonyl-Liganden” in German.

(44) Edge-bridging CO ligands have been classified as “asymmetrical” (A), “semibridging” (B), and “linear” (C).⁴¹ Among the compounds listed in the text, both (η^5 -C₅H₅)₂V₂(CO)₅ and (η^5 -C₅H₅)₃(CO)Nb(μ -CO)Co(CO)₃ belong to type B molecules.



(45) In the present example, we encounter a *symmetrical* η^2 (μ_3 -C, μ_2 -O) bridge. Note that this kind of coordination could as well be an asymmetric one with respect to the relative orientation of the CO ligand to the metals to which the oxygen acts as an edge bridge.

(46) The descriptor which gives μ_3 (η^2 -C, μ^2 -O) in our preliminary communication¹⁵ is in error. We thank Professor F. A. Cotton (Texas A&M University) for having drawn this point to our attention.

seems to be the pervasive molecular origin of CO semibridging in this kind of molecules.⁴⁷

There is yet another criterion which favors this interpretation: if simple steric reasons were to force the unique CO group toward the Nb(1) and Nb(2) centers, then one should anticipate the Nb(3)-C(33)-O(33) functionality would bend away from them. As can be seen from the drawing in Figure 4, the bridging carbonyl group is leaning toward the Nb(1)-Nb(2) vector, with the Nb(3), C(33), O(33) angle amounting to 169.6 (11)°. An on-scale model demonstrates that the CpNb(CO)₃ unit [Nb(3)] could (from a steric point of view) as well be oriented within the cluster

(47) This interpretation has first been stressed by Cotton et al. for rationalizing the structure of $(\eta^5\text{-C}_5\text{H}_5)_2\text{V}_2(\text{CO})_8$,^{8,9} and is in agreement with the high reactivity of the latter compound toward thermal dismutation.¹⁰ Remember in this context that **4** can be converted to its precursor **3** under the same conditions as $(\eta^5\text{-C}_5\text{H}_5)_2\text{V}_2(\text{CO})_8$; *cleanly* degrades to $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$.

in such a way that no semibridging CO is generated. In addition, the finding that the angles Nb(1)-C(33)-Nb(2) and Nb(1)-O(33)-Nb(2) approach orthogonality (Table IV) does certainly not occur by accident and suggests the CO ligand interacts to equal extent with Nb(1) and Nb(2) via its two orthogonal π systems.

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Crystal Structure and Low-Temperature ¹H NMR Spectrum of Tetramesityldiphosphine. Evidence for the Anti-Conformational Preference in Tetraaryldiphosphines

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Abstract: The structure of tetramesityldiphosphine (**1**) has been determined by single-crystal X-ray diffraction techniques with data collected at -35 °C by counter methods. Clear colorless crystals of **1** form in tetragonal space group *P*4₁2₁2 with *a* = 8.873 (4) and *c* = 39.272 (16) Å at -35 °C. The calculated density of 1.157 g cm⁻³, assuming 4 molecules of **1** per unit cell, agrees with the measured value of 1.15 g cm⁻³. The structure was solved by direct methods and refined by full-matrix least-squares procedures using the 1533 reflections with *I*₀/ σ (*I*₀) > 2.0. At convergence, the conventional *R* index is 0.050. The molecule possesses rigorous C₂ symmetry and exhibits an anti conformation. The slow-exchange limit 200-MHz ¹H NMR spectrum of **1** has been recorded and is consistent with a C₂ structure in solution. The molecular structure of **1** is compared to that of 1,1,2,2-tetramesityldisilane, and in most respects the structures are very similar. It is thus concluded that the same factors which dictate the conformational preference in the disilane are also dominant in **1**. Conjugation between the lone pair on phosphorus and the aryl π system does not appear to play a major role in determining the ground-state geometry of **1**.

Introduction

Tetraalkyldiphosphines and 1,1,2,2-tetraalkyldisilanes exhibit remarkably similar stereochemistries, thus leading Mislow and co-workers¹ to conclude that the electronic gauche effect² plays a negligible role in regard to the ground-state preference of tetraalkyldiphosphines. Specifically, the gauche ground-state preference of both R₂P-PR₂³⁻⁵ and R₂HSi-SiHR₂¹ compounds was found to increase as the steric bulk of the alkyl moiety increased from Me to *t*-Bu. In sharp contrast to the 1,1,2,2-

tetraalkyldisilanes, the 1,1,2,2-tetraaryldisilanes were found to exhibit a preference for the anti ground state which increased with the steric demands of the aryl group.⁶ Thus, both 1,1,2,2-tetraphenyl- and 1,1,2,2-tetramesityldisilane have been found to adopt the anti conformation in the solid state.^{6,7} However, it was not clear that this anti preference would persist in the tetraaryldiphosphines, because the conformational behavior of these compounds could be influenced by conjugation between the phosphorus lone pair and the aryl π system. Accordingly, we have performed a single-crystal X-ray diffraction analysis of tetramesityldiphosphine (**1**), the first such study of a tetraaryldiphosphine. Compound **1**⁸ was chosen primarily because definitive structural data already exist for its disilane counterpart.⁶ We have also recorded the slow-exchange limit ¹H NMR spectrum of **1** in an effort to probe its structure in solution.

Results and Discussion

Crystals of **1** form in space group *P*4₁2₁2, with four molecules per unit cell. Thus, the molecules possess rigorous C₂ symmetry.

(6) Baxter, S. G.; Mislow, K.; Blount, J. F. *Tetrahedron* **1980**, *36*, 605.

(7) However, empirical force field (EFF) calculations indicate that the energies of the gauche and anti conformers of 1,1,2,2-tetraphenyldisilane are very close.⁶ According to EFF calculations⁶ the anti conformer of 1,1,2,2-tetramesityldisilane is more stable than the gauche form by 3 kcal/mol.

(8) Stepanov, B. I.; Karpova, E. N.; Bokanov, A. I. *Zh. Obshch. Khim.* **1969**, *39*, 1544.

(1) Baxter, S. G.; Dougherty, D. A.; Hummel, J. P.; Blount, J. F.; Mislow, K. *J. Am. Chem. Soc.* **1978**, *100*, 7795.

(2) For a discussion of the gauche effect, see: (a) Wolfe, S. *Acc. Chem. Res.* **1972**, *5*, 102. (b) Radom, L.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 2371. (c) Epitotis, N. D. *Ibid.* **1973**, *95*, 3087.

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(5) (a) Brunelle, J. A.; Bushweller, C. H.; English, A. D. *J. Phys. Chem.* **1976**, *80*, 2598. (b) Aime, S.; Harris, R. K.; McVicker, E. M.; Fild, M. J. *Chem. Soc., Chem. Commun.* **1974**, 426.