10, 1486 (1971), for examples. Both sets of M–N distances are among the longest reported.
(26) D. A. Buckingham and A. M. Sargeson, *Top. Stereochem.*, **6**, 219 (1971); B. F. Anderson, J. D. Bell, D. A. Buckingham, P. J. Creswell, G. J. Gainsford, L. G. Marzilli, G. B. Robertson, and A. M. Sargeson, *Inorg. Chem.*, **16**, 3233 (1977), and references therein.
(27) D. M. Chipman and R. A. Jacobson, *Inorg. Chim. Acta*, **1**, 393 (1967); G. L. Breneman, D. M. Chipman, C. J. Galles, and R. A. Jacobson, *Inorg. Chim. Acta*, **3**, 447 (1969).
(28) M. E. Cradwick, D. Hall, and R. K. Phillips, *Acta Crystallogr., Sect. B*, **27**, 480 (1971).
(29) R. S. Shandles, R. K. Murmann, and E. O. Schlemper, *Inorg. Chem.*, **13**, 1373 (1974).
(30) J. S. Anderson, J. W. Carmichael, and A. W. Cordes, *Inorg. Chem.*, **9**, 143 (1970).
(31) F. J. Garrick, *Trans. Faraday Soc.*, **33**, 486 (1937).
(32) M. Parris, *J. Chem. Soc. A*, 583 (1967).
(33) D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *Inorg. Chem.*, **7**, 174 (1968).
(34) M. Raider and B. M. Foxman, unpublished observations; this loss has also been observed in pH titration of $(CH_3NH_2)_5CoOH_2^{3+}$: T. W. Swaddle, *Can. J. Chem.*, **55**, 3166 (1977).
(35) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution", P. Hasse and Son, Copenhagen, 1957, Chapter XI; for a further example, see A. M. Newton and T. W. Swaddle, *Can. J. Chem.*, **52**, 2751 (1974).
(36) B. M. Foxman, unpublished observations. This discussion excludes complexes of the relatively constrained ligand ethyleneimine, which may be prepared with CoA_5X^{2+} stoichiometry.
(37) S. C. Chan and S. F. Chan, *J. Chem. Soc. A*, 202 (1969).
(38) Examples: G. W. A. Fowles, P. T. Greene, and J. S. Wood, *Chem. Commun.*, 971 (1967); B. J. Russ and J. S. Wood, *ibid.*, 745 (1966).

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Bis(μ-trifluoroacetato-*O,O'*)-bis[dimethyl(4-methylpyridine)platinum](*Pt–Pt*)

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The crystal structure of the title compound has been determined from 1921 independent nonzero reflections collected with a Nonius CAD4 diffractometer using Cu Kα radiation. The compound crystallizes in the orthorhombic space group $P2_12_12_1$ with cell constants $a = 8.854$ (1) Å, $b = 15.334$ (2) Å, $c = 18.967$ (2) Å, and $Z = 4$. The structure was solved by Patterson and Fourier methods and refined to an R value of 4.9%. The Pt(1)–Pt(2) distance of 2.557 (1) Å is one of the shortest known bridged Pt–Pt bonds. The platinum atoms are octahedrally surrounded by the ligands. As a result of steric interaction between the methyl groups the octahedra are slightly deformed and rotated by 23° with respect to each other. The angles Pt–Pt–N are 169°.

Introduction

Binuclear compounds containing metal–metal bonds bridged by carboxylato groups,[1–4] triazenido groups,[5–9] and amidino groups[1,6,7,10–13] are receiving great interest lately. Best known are compounds containing quadruple metal–metal bonds[10–13] which are abundant for the complexes of metals of the Cr triad.

Recently, reports have appeared on the formation of Pt–Pt bonded compounds bridged by biphosphines,[19] sulfate groups,[14] $P_2O_7^{4-}$ groups,[15] α-pyridonato groups,[16] and carboxylato groups.[17,18]

Of particular interest are compounds of the type $[cis\text{-}R_2Pt(O_2CR')L]_2$ (R = alkyl, aryl)[17,18] and the asymmetrical complexes $Pt_2R_4(O_2CR')_2L$[18] in which one formally trivalent Pt(III) is six-coordinated and the other Pt(III) is five-coordinated.

In order to determine the influence of the bridging groups and of the number of L groups on the structure of the complexes and on the metal–metal bond length, a crystallographic study was undertaken of $[Me_2Pt(O_2CCF_3)(4\text{-}Me\text{-}py)]_2$, the results of which are given here, and recently we started an investigation of $[Ph_4Pt_2(O_2CCH_3)_2(PEt_3)]$.

Experimental Section

Weissenberg photographs suggested an orthorhombic space group and the systematic absences of $h00$ for $h = 2n + 1$, $0k0$ for $k = 2n + 1$ and $00l$ for $l = 2n + 1$ indicated space group $P2_12_12_1$.

Unit cell dimensions determined on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Cu Kα radiation and a θ–2θ scan are $a = 8.854$ (1) Å, $b = 15.334$ (2) Å, $c = 18.967$ (2) Å, and $Z = 4$.

For the intensity measurements an approximately spherical crystal was selected. A total of 1921 independent nonzero reflections were collected in the range $2 < \theta < 60°$, 1798 of which were above the significance level of 2.5σ. Experimental data were corrected for absorption using the factors for a sphere[20] with $r = 0.09$ mm ($\mu = 203.97$ cm^{-1}). Judging from the real dimensions of the crystal (0.176 × 0.180 × 0.184 mm) the systematic error not accounted for by this approximation is small.

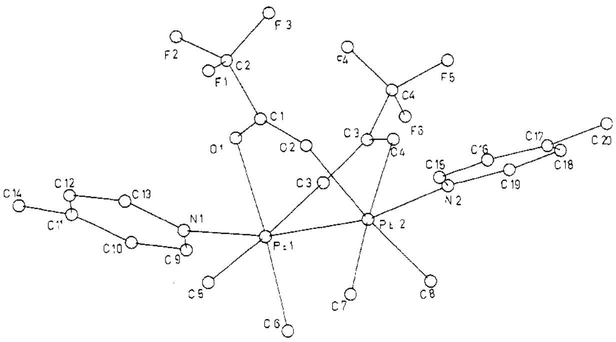

Figure 1. Molecular structure of $Pt_2(O_2C_2F_3)_2(CH_3)_4(NC_6H_7)_2$ and numbering of the atoms.

Structure Determination and Refinement

The positions of the platinum atoms were found from a sharpened Patterson function; the other nonhydrogen atoms were located in a difference Fourier synthesis. No attempt was made to locate hydrogen atoms. The refinement has been carried out by means of a block-diagonal least-squares procedure, using anisotropic temperature factors for the platinum atoms, isotropic factors for the rest of the atoms, and a Cruickshank weighting scheme. The final R value was 4.9%, and refinement of the enantiomorph resulted in an R value of 5.6%. The large thermal parameters of the F atoms suggest disorder of the CF_3 groups, a common phenomenon for these groups. The presence of disorder was confirmed in a difference synthesis; however, the information was not accurate enough to include it in the refinement.

Results and Description of the Structure

The molecular structure of $Pt_2(O_2C_2F_3)_2(CH_3)_4(NC_6H_7)_2$ is depicted in Figure 1, which also gives the numbering scheme. A stereoscopic view is given in Figure 2 and a Newman

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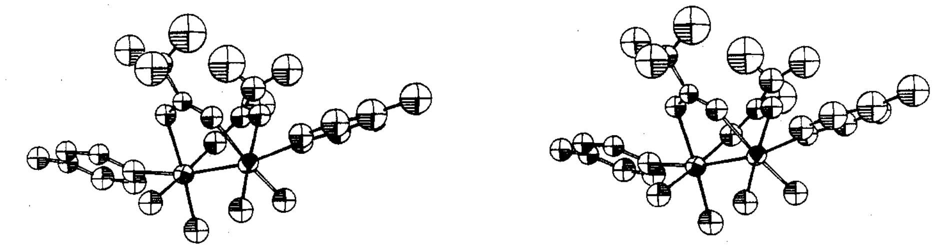

Figure 2. A stereoview of the molecule along [001].

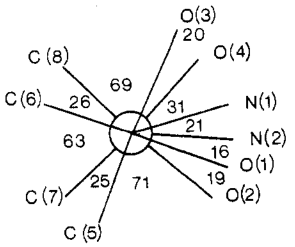

Figure 3. Newman projection along the central Pt(1)–Pt(2) bond.

Table I. Final Positional Isotropic and Anisotropic Parameters

Atom	x	y	z	10^2U
F1	−0.080 (3)	0.115 (1)	0.431 (1)	11.84
F2	−0.159 (2)	0.072 (1)	0.327 (1)	10.00
F3	−0.213 (4)	0.194 (2)	0.363 (1)	15.16
F4	−0.133 (4)	0.298 (2)	0.108 (1)	16.84
F5	−0.101 (3)	0.431 (1)	0.142 (1)	11.75
F6	0.028 (4)	0.374 (2)	0.062 (1)	14.18
C1	0.031 (2)	0.183 (1)	0.333 (1)	3.99
C2	−0.103 (3)	0.139 (2)	0.360 (1)	5.38
C3	0.081 (3)	0.323 (1)	0.177 (1)	5.20
C4	−0.032 (4)	0.356 (2)	0.125 (1)	7.33
C5	0.402 (3)	0.113 (2)	0.306 (1)	6.37
C6	0.514 (3)	0.217 (2)	0.193 (1)	7.16
C7	0.432 (3)	0.299 (2)	0.379 (1)	6.25
C8	0.403 (3)	0.404 (2)	0.258 (1)	6.41
C9	0.327 (3)	0.085 (2)	0.093 (1)	6.80
C10	0.309 (3)	0.013 (2)	0.044 (1)	6.88
C11	0.244 (3)	−0.066 (1)	0.068 (1)	5.11
C12	0.201 (3)	−0.069 (1)	0.139 (1)	5.14
C13	0.215 (3)	0.004 (1)	0.182 (1)	5.06
C14	0.223 (3)	−0.136 (2)	0.020 (1)	6.72
C15	0.168 (3)	0.418 (2)	0.450 (1)	6.04
C16	0.128 (4)	0.481 (2)	0.495 (1)	7.75
C17	0.097 (4)	0.561 (2)	0.462 (2)	9.66
C18	0.108 (3)	0.579 (2)	0.396 (1)	6.44
C19	0.152 (3)	0.510 (2)	0.354 (1)	6.08
C20	0.048 (4)	0.641 (2)	0.518 (2)	9.82
O1	0.075 (2)	0.150 (1)	0.273 (1)	4.97
O2	0.093 (2)	0.243 (1)	0.366 (1)	5.09
O3	0.177 (2)	0.265 (1)	0.154 (1)	6.14
O4	0.079 (2)	0.357 (1)	0.237 (1)	5.49
N1	0.283 (3)	0.081 (1)	0.165 (1)	6.21
N2	0.187 (3)	0.429 (1)	0.379 (1)	5.37
Pt1	0.29765 (10)	0.18876 (6)	0.23311 (4)	
Pt2	0.26153 (9)	0.32272 (5)	0.31173 (4)	

Atom	10^2U_{11}	10^2U_{22}	10^2U_{33}	10^2U_{12}	10^2U_{13}	10^2U_{23}
Pt1	4.37	4.83	3.84	0.08	0.25	0.32
Pt2	4.28	4.51	4.24	−0.35	−0.29	0.33

projection along the Pt–Pt bond is given in Figure 3. Table I contains the final positional and thermal parameters, Tables II and III show the bond lengths and angles, and Table IV lists some short intramolecular distances.

The Pt–Pt distance of 2.557 (1) Å is one of the shortest known. In the isoelectronic compound $K_2[Pt_2(SO_4)_4]\cdot 2H_2O$ where the platinum atom is also in a formal 3+ oxidation state the metal–metal bond has a length of 2.466 Å.[14] The Pt–Pt bond order of both complexes, in a simple 18-electron approach, is 1. The shortening of the metal–metal bond in the last complex is probably due to the very weak trans influence of water compared to that of picoline, although the electron-donating effect of water could not be neglected as can be seen in the anhydrous tetraacetatodichromium complex described by Cotton et al.[21] The conclusion is that in the title compound the Pt–Pt bond is longer than in $K_2[Pt_2(SO_4)_4]\cdot 2H_2O$ due to a stronger trans influence of picoline. Most other compounds with bridged Pt–Pt bonds, where the platinum atoms have an oxidation state of 2 or less, have a larger bond length varying from 2.581 (4) to 2.785 (1) Å.[22-30] Only in the case of a tetrameric platinum(II) acetate cluster has a mean value of 2.495 Å been reported.[31]

Table II. Bond Lengths (in Å) with Estimated Standard Deviations

Pt(1)-Pt(2)	2.557 (1)	C(3)–O(3)	1.30 (3)
Pt(1)–C(5)	2.03 (2)	C(3)–O(4)	1.26 (3)
Pt(1)–C(6)	2.10 (3)	C(4)–F(4)	1.29 (4)
Pt(1)–O(1)	2.19 (1)	C(4)–F(5)	1.34 (4)
Pt(1)–O(3)	2.17 (1)	C(4)–F(6)	1.32 (3)
Pt(1)–N(1)	2.09 (2)	N(1)–C(9)	1.43 (3)
Pt(2)–C(7)	2.00 (3)	C(9)–C(10)	1.44 (4)
Pt(2)–C(8)	2.04 (3)	C(10)–C(11)	1.41 (3)
Pt(2)–O(2)	2.19 (2)	C(11)–C(12)	1.40 (3)
Pt(2)–O(4)	2.21 (2)	C(11)–C(14)	1.41 (3)
Pt(2)–N(4)	2.17 (2)	C(12)–C(13)	1.39 (3)
C(1)–C(2)	1.46 (3)	C(13)–N(1)	1.36 (3)
C(1)–O(1)	1.30 (2)	N(2)–C(15)	1.36 (3)
C(1)–O(2)	1.24 (2)	C(15)–C(16)	1.35 (4)
C(2)–F(1)	1.41 (3)	C(16)–C(17)	1.40 (5)
C(2)–F(2)	1.29 (3)	C(17)–C(20)	1.66 (5)
C(2)–F(3)	1.29 (4)	C(17)–C(18)	1.28 (4)
C(3)–C(4)	1.29 (4)	C(18)–C(19)	1.38 (4)

Each Pt atom is surrounded by a slightly deformed octahedron consisting of the other platinum atom, a nitrogen atom from a picoline group, two methyl groups, and the two oxygen atoms of the bridging acetate groups.

The deformation of the octahedron is probably due to steric hindrance between the methyl groups and could be described as follows.

The Pt–Pt–C angles have increased from 90° to an average of 97.6° (Table III), owing to steric interaction between the methyl groups of Pt(1) and those of Pt(2).

The conformation about the Pt–Pt bond is determined by two opposing forces: the steric repulsion between the groups coordinated to both Pt atoms which favor a staggered conformation and the action of the acetate groups favoring the eclipsed conformation. As can be seen in Figure 3 a conformation is reached approximately midway between both.[32] A third effect of the steric interaction between the methyl groups is the deformation of the angles between the atoms perpendicular to the Pt–Pt bond. The C(7)–Pt(2)–O(2) angle (96°) is larger than the C(8)–Pt(2)–O(4) angle (89°) probably because of steric interaction of the C(5) carbon atom (see Figure 3).

Similarly the C(6)–Pt(1)–O(3) angle is increased to 95°, due to sterical interaction of C(8).

The arrangement of N(1)–Pt(1)–Pt(2)–N(2) is not linear, the angles Pt(1)–Pt(2)–N(2) and Pt(2)–Pt(1)–N(1) being 169.2 (5) and 169.0 (6)°, respectively.[32]

Pt–Pt–N angles of 180° would lead to intramolecular

Table III. Bond Angles (in deg) with Estimated Standard Deviations

Pt(1)-Pt(2)-C(7)	97.5 (7)	O(1)-C(1)-O(2)	127 (2)
Pt(1)-Pt(2)-C(8)	97.3 (7)	O(1)-C(1)-C(2)	112 (2)
Pt(1)-Pt(2)-O(2)	84.8 (4)	O(2)-C(1)-C(2)	122 (2)
Pt(1)-Pt(2)-O(4)	84.8 (4)	C(1)-C(2)-F(1)	110 (2)
Pt(1)-Pt(2)-N(2)	169.2 (5)	C(1)-C(2)-F(2)	120 (2)
Pt(2)-Pt(1)-C(5)	96.7 (7)	C(1)-C(2)-F(3)	109 (2)
Pt(2)-Pt(1)-C(6)	99.0 (7)	F(1)-C(2)-F(2)	108 (2)
Pt(2)-Pt(1)-O(2)	84.8 (4)	F(1)-C(2)-F(3)	104 (2)
Pt(2)-Pt(1)-O(4)	84.8 (4)	F(2)-C(2)-F(3)	105 (2)
Pt(2)-Pt(1)-N(1)	169.0 (5)	O(3)-C(3)-O(4)	126 (2)
O(1)-Pt(1)-O(3)	87 (1)	O(3)-C(3)-C(4)	117 (2)
O(3)-Pt(1)-C(6)	95 (1)	O(4)-C(3)-C(4)	117 (2)
C(6)-Pt(1)-C(5)	87 (1)	C(3)-C(4)-F(4)	113 (3)
C(5)-Pt(1)-O(1)	91 (1)	C(3)-C(4)-F(5)	115 (2)
O(2)-Pt(2)-O(4)	86 (1)	C(3)-C(4)-F(6)	113 (3)
O(4)-Pt(2)-C(8)	89 (1)	F(4)-C(4)-F(5)	110 (3)
C(8)-Pt(2)-C(7)	88 (1)	F(4)-C(4)-F(6)	102 (2)
C(7)-Pt(2)-O(2)	97 (1)	F(5)-C(4)-F(6)	104 (2)
N(1)-Pt(1)-O(1)	87 (1)	N(1)-C(9)-C(10)	123 (2)
N(1)-Pt(1)-O(3)	88 (1)	C(9)-C(10)-C(11)	120 (2)
N(1)-Pt(1)-C(5)	90 (1)	C(10)-C(11)-C(12)	117 (2)
N(1)-Pt(1)-C(6)	90 (1)	C(10)-C(11)-C(14)	120 (2)
N(2)-Pt(2)-O(2)	86 (1)	C(14)-C(11)-C(12)	124 (2)
N(2)-Pt(2)-O(4)	89 (1)	C(11)-C(12)-C(13)	121 (2)
N(2)-Pt(2)-C(7)	90 (1)	C(12)-C(13)-N(1)	127 (2)
N(2)-Pt(2)-C(8)	91 (1)	C(13)-N(1)-C(9)	113 (2)
Pt(1)-O(1)-C(1)	118 (1)	N(2)-C(15)-C(16)	125 (2)
Pt(1)-O(3)-C(3)	118 (1)	C(15)-C(16)-C(17)	113 (3)
Pt(2)-O(2)-C(1)	119 (1)	C(16)-C(17)-C(18)	127 (3)
Pt(2)-O(4)-C(3)	118 (1)	C(16)-C(17)-C(20)	114 (3)
Pt(1)-N(1)-C(9)	123 (2)	C(20)-C(17)-C(18)	120 (3)
Pt(1)-N(1)-C(13)	124 (1)	C(17)-C(18)-C(19)	116 (3)
Pt(2)-N(2)-C(15)	122 (2)	C(18)-C(19)-N(2)	124 (2)
Pt(2)-N(2)-C(19)	123 (1)	C(19)-N(2)-C(15)	115 (2)

Table IV. Some Short Intramolecular Distances (Å)

N(1)-O(1)	2.95 (3)	C(7)-C(8)	2.80 (3)
N(1)-O(3)	2.97 (3)	O(1)-O(2)	2.26 (2)
N(1)-C(5)	2.92 (3)	O(2)-O(4)	3.01 (2)
N(1)-C(6)	2.96 (4)	O(4)-O(3)	2.28 (2)
N(2)-O(2)	2.98 (2)	O(3)-O(1)	2.99 (2)
N(2)-O(4)	3.05 (2)	O(1)-C(5)	3.02 (3)
N(2)-C(7)	2.94 (3)	O(2)-C(7)	3.13 (3)
N(2)-C(8)	3.00 (3)	O(3)-C(6)	3.16 (3)
C(5)-C(6)	2.84 (3)	O(4)-C(8)	2.98 (3)
C(6)-C(8)	3.27 (4)		

distances between N and its adjacent methyl groups of 2.75 Å and with its adjacent acetate groups of 3.18 Å.

Pt–Pt–N angles of 169° result in N–methyl distances of approximately 2.95 Å while the contacts of the nitrogen atoms with the acetate ligands are of the same magnitude (Table IV).

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Registry No. $[Me_2Pt(O_2CCF_3)(4\text{-}Me\text{-}py)]_2$, 63056-61-1.

Supplementary Material Available: A listing of structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

References and Notes

(1) F. A. Cotton, *Chem. Soc. Rev.*, **4**, 27 (1975).
(2) J. Kuyper and K. Vrieze, *J. Organomet. Chem.*, **107**, 129 (1976).
(3) J. G. Norman, H. J. Kolari, H. B. Gray, and W. C. Trogler, *Inorg. Chem.*, **16**, 987 (1977).
(4) K. Das, E. L. Simmons, and J. L. Bear, *Inorg. Chem.*, **16**, 1268 (1977).
(5) J. Kuyper, P. I. van Vliet, and K. Vrieze, *J. Organomet. Chem.*, **96**, 289 (1975).
(6) J. Kuyper, P. I. van Vliet, and K. Vrieze, *J. Organomet. Chem.*, **105**, 379 (1976).
(7) J. Kuyper, K. Vrieze, and K. Olie, *Cryst. Struct. Commun.*, **5**, 179 (1976).
(8) R. T. Kops, A. R. Overbeek, and H. Schenk, *Cryst. Struct. Commun.*, **5**, 125 (1976).
(9) P. I. van Vliet, J. Kuyper, and K. Vrieze, *J. Organomet. Chem.*, **122**, 99 (1976).
(10) T. Inglis, H. R. Keable, M. Kilner, and E. E. Robertson, *J. Less-Common Met.*, **36**, 217 (1974).
(11) F. A. Cotton, T. Inglis, M. Kilner, and T. R. Webb, *Inorg. Chem.*, **14**, 2023 (1975).
(12) W. H. de Roode, K. Vrieze, E. A. Koerner von Gustorf, and A. Ritter, *J. Organomet. Chem.*, **135**, 183 (1977).
(13) W. H. de Roode and K. Vrieze, *J. Organomet. Chem.*, in press.
(14) G. S. Muraveiskaya, G. A. Kukina, V. S. Orlova, O. N. Evstaf'eva, and M. A. Porai-Koshits, *Proc. Acad. Sci. USSR*, **226**, 76 (1976).
(15) J. A. Stanko, results quoted by M. J. Cleare in "Platinum Coordination Complexes in Chemotherapy", T. A. Connors and J. J. Roberts, Ed., Springer-Verlag, New York, N.Y., 1974, pp 24–26.
(16) J. K. Barton, H. N. Rabinowitz, D. J. Szalda, and S. J. Lippard, *J. Am. Chem. Soc.*, **99**, 2827 (1977).
(17) J. Kuyper and K. Vrieze, *Transition Met. Chem.*, **1**, 208 (1976).
(18) B. R. Steele and K. Vrieze, *Transition Met. Chem.*, **2**, 169 (1977).
(19) M. P. Brown, R. J. Puddephatt, M. Rashidi, and K. R. Seddon, *J. Chem. Soc., Dalton Trans.*, 951 (1977).
(20) "International Tables for X-ray Crystallography", Vol. II, Kynoch Press, Birmingham, England, 1959, Table 5.3.6B.
(21) F. A. Cotton, C. E. Rice, and G. W. Rice, *J. Am. Chem. Soc.*, **99**, 4704 (1977).
(22) A. C. Skapski and P. G. H. Troughton, *J. Chem. Soc. A*, 2772 (1969).
(23) N. J. Taylor, P. C. Chieh, and A. J. Carty, *J. Chem. Soc., Chem. Commun.*, 448 (1975).
(24) M. Green, J. A. K. Howard, A. Laguna, M. Murray, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 451 (1975).
(25) V. G. Albano and G. Ciani, *J. Organomet. Chem.*, **66**, 311–320 (1974).
(26) K. K. Cheung, R. J. Cross, K. P. Forrest, R. Wardle, and M. Mercer, *Chem. Commun.*, 875 (1971).
(27) J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **94**, 1009 (1972).
(28) K. W. Browall, L. V. Interrante, and J. S. Kasper, *J. Am. Chem. Soc.*, **93**, 6289 (1971).
(29) R. G. Vranka, L. F. Dahl, P. Chini, and J. Chatt, *J. Am. Chem. Soc.*, **91**, 1574 (1969).
(30) K. P. Wagner, R. W. Hess, P. M. Treickel, and J. C. Calabrese, *Inorg. Chem.*, **14**, 1121 (1975).
(31) M. A. A. F. de C. T. Carrondo and A. C. Skapski, *J. Chem. Soc., Chem. Commun.*, 410 (1976).
(32) H. Schumann, J. Opitz, and J. Pickardt, *J. Organomet. Chem.*, **128**, 253 (1977).