kcal/mol at 300 K). This change is small compared with the calculated solvation enthalpy (−23 kcal/mol) at infinite dilution.[10]

Comparison of the internal entropy differences of the conformers in solution shows that the values are of the same magnitude as those found in vacuum (see Table I). The solvated polyproline conformation appears to have somewhat less freedom than the α-helical conformer, which is very similar in entropy to the C_7^{eq} conformer.

This study of a peptide model system has demonstrated that molecular dynamics simulations can be used to estimate the configuration entropy differences in conformational transitions and in solvation processes. Such internal entropy changes have to be included in any calculations of the free energy differences between conformers.[12,13]

Registry No. $CH_3CONHCHCH_3CONHCH_3$, 22715-68-0.

(12) Mezei, M.; Mehrotra, P. K.; Beveridge, D. L., private communication.
(13) Pettitt, M., Karplus, M., unpublished results.

Intramolecular Reductive Elimination of Methane from a Dinuclear Palladium Complex Containing Methyl and Hydride on Adjacent Palladium Centers

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Dinuclear elimination of groups from two different metal atoms involving the formation of metal-metal bonds or bridged metal centers is an important step in many reactions that are catalyzed by transition metals.[1] Although intermolecular dinuclear reductive elimination mechanisms have been established for several reactions,[2] only rarely have the corresponding intramolecular eliminations been investigated.[3] We report herein the preparation, isolation, and structure of a dinuclear palladium complex containing methyl and hydride on adjacent palladium atoms and its facile 1,1-dinuclear intramolecular elimination of methane.

Although a relatively large number of dinuclear platinum complexes containing two bridging bis(diphenylphosphino)methane ligands and alkyl groups σ-bonded to platinum are known, there are relatively few examples of similar dinuclear palladium complexes.[4–6] The reaction of an equimolar amount of trimethylaluminum with the palladium(I) chloride dimer $Pd_2Cl_2(\mu\text{-}dppm)_2$ [dppm=bis(diphenylphosphino)methane] (**1**)[7] at −78 °C in methylene chloride gave an intermediate (**2**) which could not be isolated (Scheme I) but was characterized by its ¹H and ³¹P{¹H} spectra. The ³¹P{¹H} spectrum of **2**, analyzed as an AA′BB′ spin

(1) For several examples, see: Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books, Mill Valley, CA, 1980; Chapter 8.
(2) Norton, J. R. *Acc. Chem. Res.* **1979**, *12*, 139.
(3) Kazi, A. A.; Hill, R. H.; Puddephatt, R. J. *Can. J. Chem.* **1984**, *62*, 2029 and references therein.
(4) Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, *12*, 99.
(5) Balch, A. L. *Adv. Chem. Ser.* **1982**, *196*, 243.
(6) (a) Olmstead, M. M.; Farr, J. P.; Balch, A. L. *Inorg. Chim. Acta* **1981**, *52*, 47. (b) Balch, A. L.; Hunt, C. T.; Lee, C.-L.; Olmstead, M. M.; Farr, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 3764. (c) Lee, C.-L.; Hunt, C. T.; Balch, A. L. *Organometallics* **1982**, *1*, 824.
(7) (a) Colton, R.; Farthing, R. H.; McCormick, M. J. *Aust. J. Chem.* **1973**, *26*, 2607. (b) Holloway, R. G.; Penfold, B. R.; Colton, R.; McCormick, M. J. *J. Chem. Soc., Chem. Commun.* **1976**, 485. (c) Benner, L. S.; Balch, A. L. *J. Am. Chem. Soc.* **1978**, *100*, 6099. (d) Brant, P.; Benner, L. S.; Balch, A. L. *Inorg. Chem.* **1979**, *18*, 3422. (e) Hunt, C. T.; Balch, A. L. *Inorg. Chem.* **1981**, *20*, 2267. (f) Balch, A. L.; Benner, L. S. *Inorg. Synth.* **1982**, *21*, 47. (g) Pringle, P. G.; Shaw, B. L.; *J. Chem. Soc., Chem. Commun.* **1982**, 81. (h) Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1983**, 889.
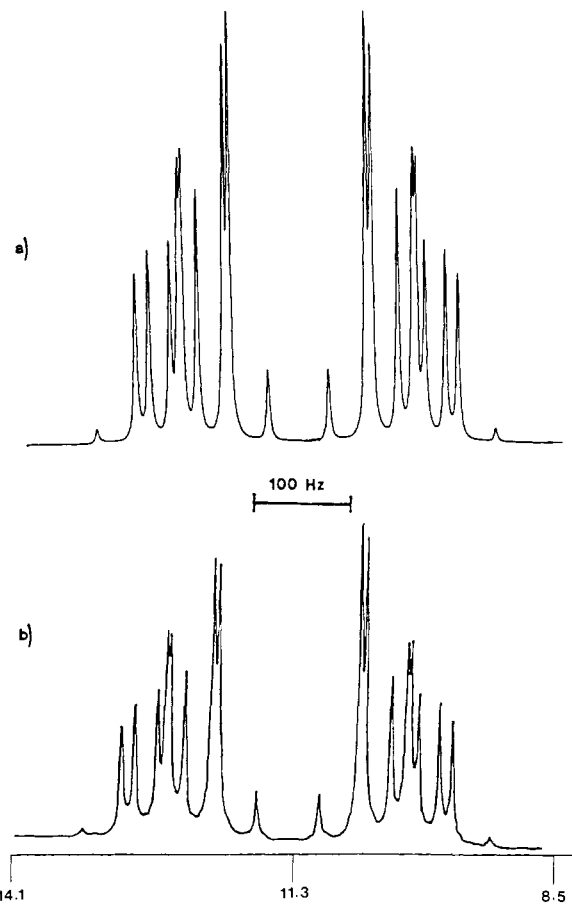

Figure 1. ³¹P{¹H} NMR (81.015 MHz) of **2**. (a) Simulated spectrum; (b) spectrum of **2** at −80 °C in CD_2Cl_2.
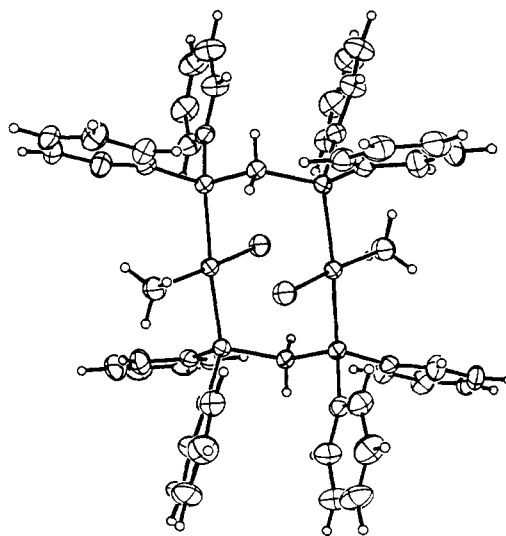

Figure 2. X-ray Structure of **3**.

system, is shown (Figure 1) along with the calculated spectrum.

An ambient temperature, **2** disproportionated to a palladium(0) complex (**4**) and **3**. The X-ray structure of **3** (Figure 2) verified a face-to-face dimer with methyl groups in the anti geometry. The palladium(0) complex **4** reacted with methylene chloride to give the A-frame methylene-bridged dimer **5**. The reaction of methylene chloride with $Pd_2(dppm)_3$ to form **5** has been reported to proceed very slowly.[7b] A faster reaction with **4** was observed, apparently because it is a more coordinatively unsaturated palladium(0) species. Complex **3** is not available via the oxidative addition of methyl chloride to $Pd_2(dppm)_3$.

Intermediate complex **2** reacted with ethanol at −78 °C to give the dinuclear palladium complex **6-H**, containing methyl and

Scheme I

6-D

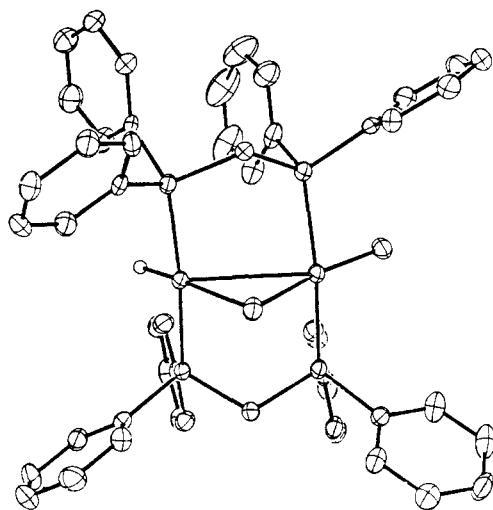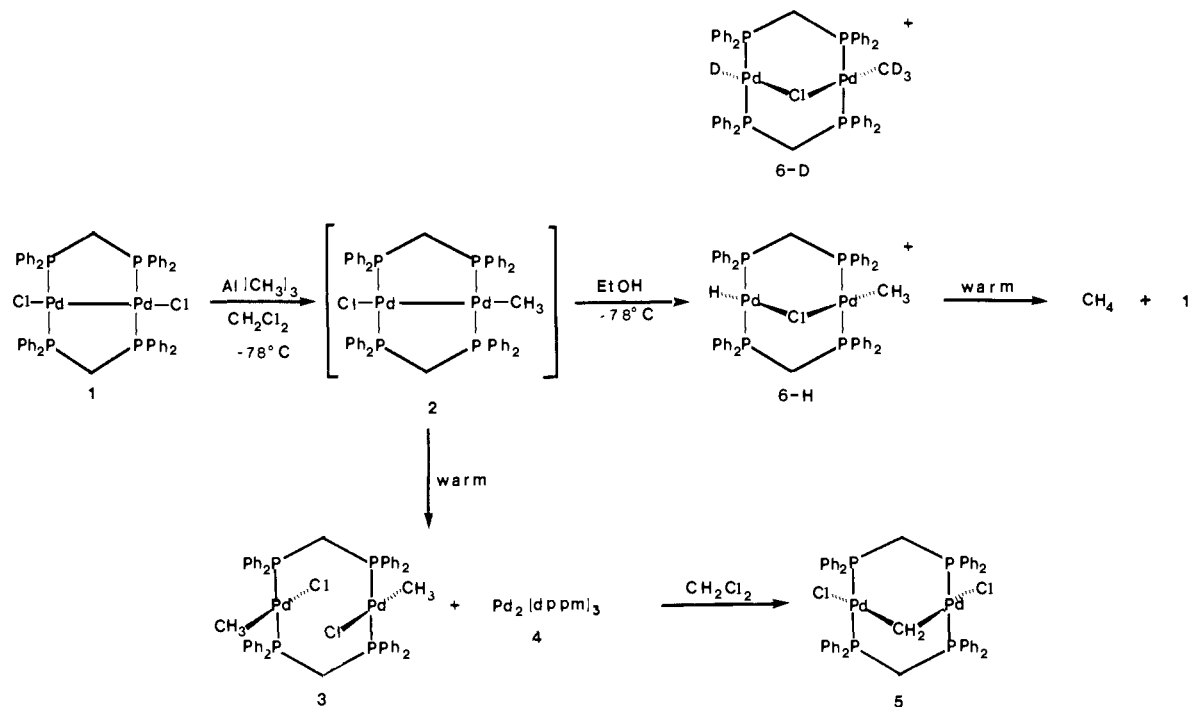1 → 2 → 6-H → warm → CH_4 + 1

3   4   5

Figure 3. X-ray Structure of 6-H.

hydride on different palladium atoms. Complex 6-H, isolated as its tetraphenylborate salt, was fully characterized[8] including its X-ray structure (Figure 3). When a solution of 6-H, as its chloride salt, was warmed to −20 °C, methane was produced quantitatively along with the palladium(I) chloride dimer 1. When 6-H, as its tetraphenylborate salt, was warmed (40 °C) in solution, a quantitative evolution of methane (Toepler pump analysis, GC, mass spectrum) occurred at 55 °C. However, addition of LiCl to the solution of the tetraphenylborate salt allowed the reductive elimination to take place at lower temperatures (−20 °C). In no case was ethane or hydrogen evolved (NMR, GC, mass spectrum).

The corresponding deuterated complex (6-D), containing deuteride on one palladium and trideuteriomethyl on the other, was prepared with perdeuteriotrimethylaluminum[9] and ethanol-d_1. Reductive elimination from 6-D gave a quantitative yield of CD_4. A solution containing equimolar amounts of 6-H and 6-D produced only CH_4 and CD_4 (m/e 20, 16, but no 19). Thus, the reductive

Scheme II

6-H   a ⇌ b

d ⇌ c
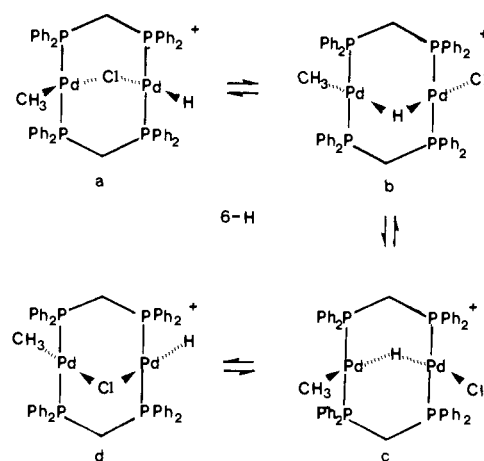
elimination is strictly intramolecular.[10]

Several observations on the decomposition of 6-H are consistent with a 1,1-reductive elimination of methane. A dinuclear 1,2 elimination is theoretically symmetry forbidden; extended Hückel calculations predict a minimum activation energy of approximately 65 kcal/mol for the elimination of dihydrogen from adjacent metals, even when the hydrogen atoms undergo a prior bending toward each other to establish the final dihydrogen geometry.[11] In addition, the two methylene protons on dppm in the A-frame dimer 5 have different chemical shifts, (δ 2.83 and 2.58) but the methylene protons on dimers 6-H and 6-D are identical[12] (δ 4.57), even at −100 °C (200 MHz). The fluxionality of these complexes provides a pathway for the reductive elimination of methane whereby methyl and hydride become attached to the same palladium. Of the number of mechanisms for the A-frame inversion of platinum complexes of the type $[Pt_2(\mu\text{-dppm})_2(\mu\text{-Y})X_2]$ that have been considered, inversion of hydride through the platinum–platinum center is that most consistent with the available data.[13] A rapid equilibrium (Scheme II) involving an exchange

(8) ^{1}H NMR (CD_2Cl_2) δ 3.91 (qi, $J = 4.0$ Hz, 4 H), 0.65 (t, $J = 6.0$ Hz, 3 H), −12.42 (t, $J = 10.0$ Hz, 1 H); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 20.79, 16.27 (AA′BB′, |$J_{AA'}J_{BB'}$| = 9, J_{AB} = 50, $J_{AB'}$ = 3 Hz).
(9) Pasynkiewicz, S.; Boleslawski, M. *J. Organomet. Chem.* **1970**, *25*, 29.

(10) Attempts to establish a kinetic isotope effect proved ambiguous.
(11) Trinquier, G.; Hoffmann, R. *Organometallics* **1984**, *3*, 370.
(12) This equivalence of the methylene proton resource is observed in CD_2Cl_2 for the chloride and tetraphenylborate salts of 6-H and 6-D and in THF-d_8 for the borate salts of 6-H and 6-D.

of the chloride bridge with a hydride bridge followed by inversion of hydride (**6-H$_b$** ⇌ **6-H$_c$**)—or the formation of a linear hydride bridge—and reformation of the chloride bridge would account for the equivalence of the methylene hydrogens on dppm. The palladium–palladium distance in **6-H**, 3.01 Å, is sufficient to accommodate this process (Pd–H = 1.56 ± 0.04 Å). This not only would lead to the observed equivalence but also provides a mechanism by which hydride and methyl become bonded to the same palladium. In fact, an intermediate consistent with a methyl and a hydride ligand on the same palladium center is observed for the chloride salt of **6-H** during the reductive elimination.[14] The role of the LiCl is not completely understood, but apparently the terminal bonding of chloride is effective in shifting the equilibrium to the complex with both methyl and hydride on one palladium. The hydride and methyl ligands in complexes **6-H$_b$** and **6-H$_c$**, however, are trans, and an isomerization to a cis complex would be required prior to reductive elimination,[15] probably by dissociation of one phosph. ˙ of dppm.[16] The observation of two new ³¹P NMR signals at δ 3 and +16 during the course of the reaction is consistent with ι h a species.

The reductive elimination re ˙ions of other dinuclear palladium complexes containing hydride a˳ ˎrganic ligands and the reaction of **6-H** with carbon monoxide a˷ˡ other small molecules will be reported in the future.

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(13) Puddephatt, R. J.; Azam, K. A.; Hill, R. H.; Brown, M. P.; Nelson, C. D.; Moulding, R. P.; Seddon, K. R.; Grossel, M. C. *J. Am. Chem. Soc.* **1983**, *105*, 5642.

(14) ¹H NMR (CD₂Cl₂, -25 °C) δ -0.49 (t, *J* = 4 Hz, 3 H), -10.92 (t, *J* = 11 Hz, 1 H). The coupling between the hydride and the methyl protons could not be resolved.

(15) Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857.

(16) For a related Pt complex containing a μ-dppm and a η'-dppm ligand, see: Braunstein, P.; de Meric de Bellefon, C.; Lanfranchi, M.; Tiripicchio, A. *Organometallics* **1984**, *3*, 1772.


A New Type of Carbene Catalyst. Direct Evidence for the Involvement of Coordinated Carbenes in a Cluster-Catalyzed Transalkylation Reaction between Tertiary Amines

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Catalytic transalkylation of tertiary amines is a new and potentially valuable method for the synthesis of unsymmetrical tertiary amines (eq 1, R, R' = alkyl). C–H activations in the

$$NR_3 + NR'_3 \rightleftharpoons NR_2R' + NRR'_2 \qquad (1)$$
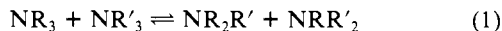
alkyl groups occur in conjunction with the transalkylation, and this has led to the proposal that iminium ion complexes are important intermediates.[1-4] We now wish to report on the preparation and characterization of an unusual amino–carbene cluster complex that is also a very effective catalyst for the transalkylation reaction.

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(1) Murahashi, S.-I.; Hirano, T.; Yano, T. *J. Am. Chem. Soc.* **1978**, *100*, 348.

(2) (a) Laine, R. M.; Wilson, R. B., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 361. (b) Shvo, Y.; Laine, R. M. *J. Chem. Soc., Chem. Commun.* **1980**, 753.

(3) Murahashi, S.-I.; Yoshimura, N.; Tsumiyama, T.; Kojima, R. *J. Am. Chem. Soc.* **1983**, *105*, 5002.

(4) Laine, R. M.; Thomas, D. W.; Cary, L. W. *J. Am. Chem. Soc.* **1982**, *104*, 1763.
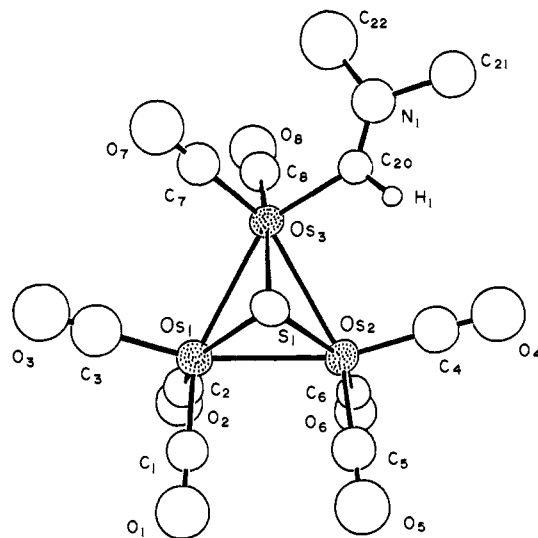

Figure 1. ORTEP drawing of one of the two symmetry independent molecules found in the crystal of Os₃(CO)₈[C(H)NMe₂](μ-H)₂(μ₃-S) (**1**).

Under an atmosphere of NMe₃ at 125 °C in octane solvent the sulfido cluster Os₃(CO)₉(μ₃-CO)(μ₃-S)[5] adds one formula equivalent of NMe₃ to yield the new compound Os₃(CO)₈[C-(H)NMe₂](μ-H)₂(μ₃-S) (**1**) (31% yield). Compound **1** has been characterized by IR and ¹H NMR spectroscopies and by a single-crystal X-ray diffraction analysis.[6] The compound crystallizes in the triclinic space group P$\bar{1}$ with two independent molecules in the asymmetric crystal unit. Both molecules are very similar structurally and an ORTEP drawing of one of these is shown in Figure 1.[7] The molecule consists of a triangular cluster of three osmium atoms bridged by a triply bridging sulfido ligand. The presence of two inequivalent hydride ligands was established by ¹H NMR spectroscopy, δ -20.38, -21.18. They were not observed in the crystallographic analysis, but the significant elongation of two of the three metal–metal bonds (e.g., Os(1)–Os(3) = 2.911 (1) Å, and Os(2)–Os(3) = 2.922 (1) Å vs. Os(1)–Os(2) = 2.768 (1) Å) indicates that they are bridging these two bonds. This portion of the molecule is very similar to that of Os₃(CO)₉(μ₂-H)₂(μ₃-S).[8] The most interesting and unusual feature of compound **1** is the presence of a (dimethylamino)carbene ligand, C(H)NMe₂. Although not unprecedented, secondary amino-carbene ligands are not commonly occurring.[9,10] The molecular dimensions of this ligand are not exceptional and the nitrogen atom

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(5) Adams, R. D.; Horvath, I. T.; Kim, H. S. *Organometallics* **1984**, *3*, 548.

(6) IR spectra were taken on a Nicolet 5-DXB FT-IR spectrometer in hexane solvent: ν(CO) (cm⁻¹) 2083.9 (m), 2047.1 (s), 2034.7 (m), 2002.9 (s), 1986.4 (m), 1973.7 (w), 1964.6 (w). ¹H NMR spectra were run on an IBM NR-80 spectrometer in CDCl₃ solvent δ 11.18 (s, br, NCH), 3.64 (d, *J*$_{HH}$ = 0.8 Hz, NCH₃), 3.56 (d, *J*$_{HH}$ = 0.8 Hz, NCH₃), -20.38 (s, br, OsH), -21.18 (s, OsH). Pale yellow crystals of compound **1** were grown by slow evaporation of solvent from cyclohexane solution at -5 °C. These crystals belong to the triclinic space group P$\bar{1}$, *a* = 8.703 (1) Å, *b* = 12.226 (2) Å, *c* = 18.980 (4) Å, α = 85.30 (1)°, β = 78.65 (1)°, γ = 72.29 (1)°, *V* = 1885.7 (7) Å³, *Z* = 4, ρ$_{calcd}$ = 3.12 g/cm³. Diffraction data were collected on an Enraf-Nonius CAD-4 automatic diffractometer using Mo K$_α$ radiation and the ω-scan technique. Structure-solving calculations were performed on a Digital Equipment Corp. PDP 11/60 computer by using the Enraf-Nonius program library SDP-Plus. The structure was solved by a combination of Patterson and difference Fourier techniques. The data were corrected for absorption (μ$_t$ = 203 cm⁻¹), and the structure was refined by using 3554 reflections (*F²* ≥ 3.0σ(*F²*)) to yield the final residuals *R* = 0.043 and *R$_w$* = 0.052.

(7) Selected interatomic distances (Å) and angles (deg) for **1**: Os(1)–Os(2) = 2.768 (1), Os(1)–Os(3) = 2.911 (1), Os(2)–Os(3) = 2.922 (1), Os(4)–Os(5) = 2.920 (1), Os(4)–Os(6) = 2.918 (1), Os(5)–Os(6) = 2.773 (1), Os(3)–C(20) = 2.026 (15), Os(4)–C(17) = 2.04 (2), C(20)–N(1) = 1.27 (2), C(17)–N(2) = 1.26 (2); Os(3)–C(20)–N(1) = 135 (1), Os(4)–C(17)–N(2) = 136 (1).

(8) Johnson, B. F. G.; Lewis, J.; Pipard, D.; Raithby, P. R.; Sheldrick, G. M.; Rouse, K. D. *J. Chem. Soc., Dalton Trans.* **1979**, 616.

(9) Hartshorn, A. J.; Lappert, M. F.; Turner, K. *J. Chem. Soc., Dalton Trans.* **1978**, 348.

(10) Clark, G. R. *J. Organomet. Chem.* **1977**, *134*, 51.