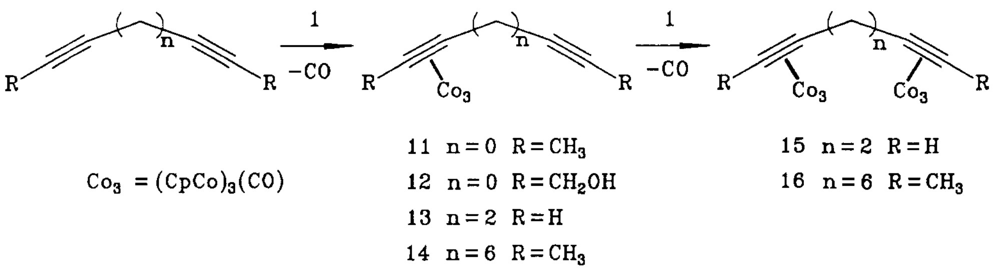
ORGANOMETALLICS

Carbon-carbon coupling between olefinic C atoms on a cluster as a Lewis acid-base reaction

Daniel Heineke, and Heinrich Vahrenkamp

Organometallics, **1990**, 9 (5), 1697-1699• DOI: 10.1021/om00119a051 • Publication Date (Web): 01 May 2002

Scheme III



dicates an edge-bridging geometry. Similar spectroscopic characteristics have been reported for a trirhodium bis(pentafluorophenyl)acetylene complex, $(CpRh)_3(CO)(C_6F_5C_2C_6F_5)$,[10] in which both the acetylene and the edge bridging carbonyl ligand are on the same side of the trirhodium plane. We assume that **10** has the same overall structure.[11]

Heating **10** to 100 °C in toluene causes clean, irreversible transformation to **5**.[12] As this isomerization takes place, an NMR study reveals that between 70 and 100 °C the two downfield Cp signals of **10** coalesce to form a single peak.[13] The energy barrier for this process is estimated to be 17.5 kcal/mol.[14] The isomerization of **10** to **5** follows first-order kinetics in toluene-d_8 ($t_{1/2}$ = 56 min, 80 °C). NOE enhancements are observed only for the downfield Cp signals of **10** at 4.76 and 4.63 ppm when the *tert*-butyl signal was irradiated.[15] Irradiation of each of the Cp signals at 40 and 60 °C gave rise to magnetization transfer only between the signals at 4.76 and 4.63 ppm.

These data are consistent with the following two processes (Scheme II). The first involves a "windshield wiper" movement of the unsubstituted end of the alkyne between two Co–Co edges of the Co_3 triangle with synchronous movement of the carbonyl ligand between the same two edges.[16] This process equilibrates the two enantiomers of **10** and accounts for the coalescence behavior observed in the NMR spectrum. The second process is irreversible and involves the movement of the carbonyl ligand from a Co–Co edge to a triply bridging coordination geometry on the Co_3 face opposite the alkyne ligand. The temperature at which the isomerization takes place is far above that at which these isomers are initially formed from **1**. Preliminary experiments indicate that neither added CO nor excess alkyne catalyze the isomerization of **10** to **5**.

Clean, sequential mono- and diaddition of **1** to diynes has also been observed as illustrated in Scheme III.

In all cases the first addition of **1** to a diyne yields the fluxional adduct analogous to **5**. The second addition yields either the fluxional or the static adduct (e.g., **10**) depending on the steric bulk and proximity of the substituents on the triple bond.[17] The examples above illustrate the scope of this reaction with respect to the alkyne substrate. Similar products are obtained when mixed metal analogues to **1** are exposed to alkynes.[2a] We are currently investigating schemes for the remote functionalization and linking of these and other "$(CpM)_3$"–alkyne adducts to produce charge-transfer species and organometallic polymers.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Johnson Matthey Co. for their generous loan of precious-metal starting materials.

Registry No. **1**, 121232-36-8; **2**, 126217-64-9; **3**, 126217-65-0; **4**, 126217-66-1; **5**, 126217-67-2; **6**, 126217-68-3; **7**, 126217-69-4; **8**, 126217-70-7; **9**, 126217-71-8; **10**, 126217-72-9; **11**, 126217-73-0; **12**, 126217-74-1; **13**, 126217-75-2; **14**, 126217-76-3; **15a**, 126217-77-4; **15b**, 126217-79-6; **16**, 126217-78-5; $HC{\equiv}CH$, 74-86-2; $MeC{\equiv}CMe$, 503-17-3; $EtC{\equiv}CEt$, 928-49-4; $(CH_3)_3CC{\equiv}CH$, 917-92-0; $PhC{\equiv}CH$, 536-74-3; $PhC{\equiv}CPh$, 501-65-5; $HOCH_2C{\equiv}CCH_2OH$, 110-65-6; $CH_3CO_2C{\equiv}CCO_2CH_3$, 762-42-5; $CH_3C{\equiv}CC{\equiv}CCH_3$, 2809-69-0; $HOCH_2C{\equiv}CC{\equiv}CCH_2OH$, 3031-68-3; $HC{\equiv}C(CH_2)_2C{\equiv}CH$, 628-16-0; $CH_3C{\equiv}C(CH_2)_6C{\equiv}CCH_3$, 31699-38-4.

Supplementary Material Available: Tables of crystal data and summary of data collection and refinement, ORTEP illustration showing numbering scheme for all atoms, and tables of fractional coordinates, thermal parameters, anisotropic thermal parameters, interatomic distances, and interatomic angles for **4** and spectroscopic data for complexes **11–16** (9 pages); a listing of structure factors for **4** (9 pages). Ordering information is given on any current masthead page.

---

(10) Trinh-Toan, P. W.; Broach, S. A.; Gardner, M. R.; Rausch, M. R.; Dahl, L. F. *Inorg. Chem.* **1977**, *16*, 279–289.

(11) The position of the carbonyl ligand relative to the unsymmetrical alkyne in **10** is as yet undetermined. Assuming the carbonyl and acetylene ligands are on the same side of the tricobalt plane, the carbonyl ligand should bridge the edge opposite the alkyne ligand as observed in the rhodium complex.

(12) One other system has been described in which the static and dynamic isomers of this type of trinuclear complex may be equilibrated: Dickson, R. S.; Mok, C.; Pain, G. *J. Organomet. Chem.* **1979**, *166*, 385–402.

(13) The coalescence phenomenon is completely reversible and distinct from the isomerization of **10** to **5**.

(14) From line width and separation of signals for the static, low-temperature limit and the coalescence temperature.

(15) Corresponding NOE effects were observed for the Cp signal at 4.52 ppm when the acetylene proton signal was irradiated.

(16) The exact mechanistic sequence for the this process and the irreversible isomerization of **10** to **5** remain unclear. Investigations are in progress to define more clearly this behavior.

(17) Monoaddition of **1** to 1,5-hexadiyne gives rise to the fluxional adduct. Diaddition gives rise to mixtures of both the fluxional–fluxional and fluxional–static adducts which have been isolated, separated, and characterized. Spectroscopic data (IR, ^1H, ^{13}C NMR) for complexes **11–16** are provided in the supplementary material.

Carbon–Carbon Coupling between Olefinic C Atoms on a Cluster as a Lewis Acid–Base Reaction

Daniel Heineke and Heinrich Vahrenkamp*

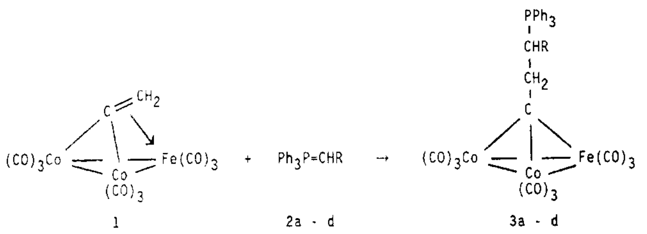
Institut für Anorganische und
Analytische Chemie der Universität Freiburg
D-7800 Freiburg, Germany

Received December 11, 1989

Summary: The CH_2 group of the nonpolar cluster compound $FeCo_2(CO)_9(\mu_3\text{-}\eta^2\text{-}C{=}CH_2)$ as a Lewis acid has been attached to the methylene group of the neutral phosphorus ylides $Ph_3P{=}CHR$ (R = H, $SiMe_3$, C(O)Ph, COOEt) as a Lewis base. This is the first case of a Lewis acid–base combination of two uncharged methylene units resulting in an isolable primary product.

0276-7333/90/2309-1697$02.50/0 © 1990 American Chemical Society

Scheme I



a: R = H, b: R = $SiMe_3$, c: R = C(O)Ph, d: R = COOEt

Thinking in terms of isoelectronic relations has mainly fertilized main-group element chemistry, e.g., the investigation of boron–nitrogen compounds in relation to their carbon–carbon analogues. The reverse approach, i.e., seeking pathways in organic chemistry derived from boron–nitrogen systems, is quite uncommon. We wish to present here a result obtained through this way of thinking, namely, a C–C bond-forming reaction that is analogous to the formation of amine boranes by combination of BR_3 and NR_3.

The simplest organic Lewis acids and bases related to BH_3 and NH_3 would be CH_3^+ and CH_3^-. While these cannot be handled as such in solution, uncharged derivatives of the latter are available in the form of the phosphorus ylides, the simplest of which, e.g., $Me_3P{=}CH_2$,[1] are nonpolar and volatile. It is well-known that phosphorus ylides are strongly nucleophilic carbon bases having a rich coordination chemistry.[2] They also readily attack electrophilic methylene units such as in Michael reactions,[3] but the primary addition products do not persist due to rearrangement reactions.[4,5]

On the other hand, there is quite a number of organometallic compounds with ligands containing olefinic carbon atoms that are electrophilic, such as in carbene,[6] olefin,[7] or vinylidene/allenylidene[8] complexes. Additions of nucleophiles, e.g., phosphines, to such ligands have been reported,[6-8] and the cationic olefin complex $[Cp(CO)(PPh_3)Fe(C_2H_4)]^+$ has been found to give the cationic σ-alkyl complex $[Cp(CO)(PPh_3)FeCH_2CH_2CH_2PPh_3]^+$ with the ylide $Ph_3P{=}CH_2$.[9] We have prepared a series of neutral trimetallic vinylidene complexes[10] and observed that they are electrophilic at the outer C atom of the μ_3-C=CHR ligand. Thus $FeCo_2(CO)_9(\mu_3\text{-}\eta^2\text{-}C{=}CH_2)$ (1) adds phosphines to form the betaine-type cluster compounds $FeCo_2(CO)_9(\mu_3\text{-}\eta^1\text{-}CCH_2PR_3)$.[11]

In continuation of these investigations we have now found that the cluster 1 can be used as a neutral Lewis acid reacting with the phosphorus ylides 2 as neutral Lewis bases, forming the C–C coupled products 3 according to Scheme I.

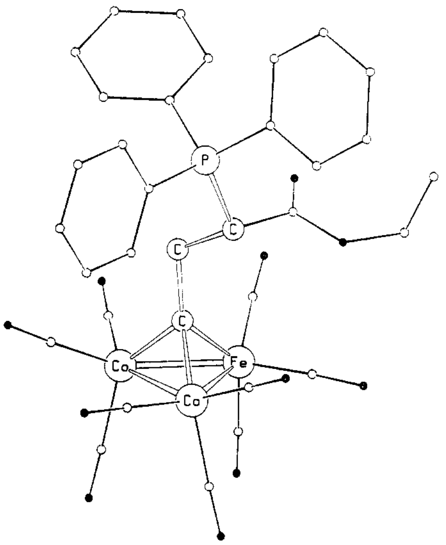


Figure 1. Schematic SCHAKAL plot of the molecular structure of **3d** (important bond lengths (pm): Fe–Co 249.1/249.1 (3), Co–Co 251.1 (3), Fe–μ_3-C 193 (1), Co–μ_3-C 188/190 (1), μ_3-C–C 154 (2), C–C 156 (2), C–P 185 (1)).

The reactions were performed on a 0.2–0.5 mmol scale in 25 mL of *n*-hexane (for **2a** and **2b**) and THF (for **2c** and **2d**). The adducts **3a** and **3b** were precipitated immediately, and **3c** and **3d** after addition of *n*-pentane, in essentially quantitative yields.[12] All four cluster compounds 3 show very similar IR spectra with ν(CO) bands at ca. 2065 m, 2010 vs, 1995 vs, 1985 vs, and 1915 w cm^{-1} in CH_2Cl_2. The band pattern resembles that of the starting cluster[10] but is shifted by about 45 cm^{-1} to lower wavenumbers. The ^{1}H NMR data of **3a–d** are less informative due to their complexity.[13] The high polarity of the adducts 3 as evidenced by their insolubility in hydrocarbons suggests a zwitterionic formulation with a positive charge on the phosphorus atom and a negative charged delocalized over the three metal atoms. This is in accord with the IR patterns (see above).

The constitution of the new cluster compounds 3 was ascertained by a crystal structure determination of **3d**.[14] As Figure 1 shows, the complex contains an alkyl chain attached on one side to the phosphonium group and on the other side to the μ_3-bridging carbon atom. The overall geometry of the $FeCo_2(CO)_9C\text{-}CH_2$ unit closely resembles that of the cluster $Co_3(CO)_9CCH_3$.[15] The μ_3-C–C axis is nearly vertical (83°) with respect to the $FeCo_2$ plane. The two C–C bond lengths in the carbon chain (154 and 156 (2) pm) correspond to single bonds, as does the P–C bond length in the chain (185 (1) pm). The C–C–C and C–C–P bond angles along the chain (113 and 108 (1)°) are, as expected, close to the tetrahedral angle. The molecular

---

(1) Schmidbaur, H. *Adv. Organomet. Chem.* **1976**, *14*, 205.

(2) Schmidbaur, H. *Angew. Chem.* **1983**, *95*, 980; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 907.

(3) Bestmann, H. J.; Zimmermann, R. *Top. Curr. Chem.* **1971**, *20*, 1.

(4) Bestmann, H. J.; Zimmermann, R. In *Organic Phosphorus Compounds*; Kosolapoff, G. M., Maier, L., Eds.; Wiley: New York, 1972; Volume 3, p 1.

(5) Bestmann, H. J.; Zimmermann, R. In *Organische Phosphorverbindungen I (Houben-Weyl's Methoden der Organischen Chemie)*; Regitz M., Ed.; Thieme Verlag: Stuttgart, FRG, 1982; Volume E1, pp 704–710.

(6) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, FRG, 1983.

(7) Lennon, P.; Madhavarao, M.; Rosan, A.; Rosenblum, M. *J. Organomet. Chem.* **1976**, *108*, 93, and references therein.

(8) Bruce, M. I.; Swincer, G. *Adv. Organomet. Chem.* **1983**, *22*, 60.

(9) Reger, D. L.; Culbertson, E. C. *J. Organomet. Chem.* **1977**, *131*, 297.

(10) Albiez, T.; Bernhardt, W.; von Schnering, C.; Roland, E.; Bantel, H.; Vahrenkamp, H. *Chem. Ber.* **1987**, *120*, 141.

(11) Albiez, T.; Vahrenkamp, H. *Angew. Chem.* **1987**, *99*, 561; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 572.

(12) Except for **3a**, which slowly decomposes in solution, the adducts were recrystallized from CH_2Cl_2/*n*-pentane at −25 °C, yielding 70–90% of the analytically pure products.

(13) All protons on the CH_2–CHR unit are coupled to phosphorus with additional splittings arising due to the chirality of **3b–d**. So far the multiline patterns (in $CDCl_3$) of **3a** (3.8–4.4 ppm), **3b** (3.9–4.4 ppm, $SiMe_3$ singlet at 0.35 ppm), **3c** (4.1–4.9 ppm), and **3d** (3.9–4.8 ppm, CH_3 triplet at 0,96 ppm) were only partially assigned.

(14) Crystal data: tetragonal, $I4_1/a$, $a = b = 3471.5$ (9), $c = 1261.2$ (7) pm, $Z = 16$; 2908 unique reflections; anisotropic refinement; 308 variables; R (unit weights) = 0.074. Further details of the structure determination can be obtained from the Fachinformationszentrum Karlsruhe, 7514 Eggenstein-Leopoldshafen 2, West Germany, upon quotation of the depository no. CSD-54075, the authors and the journal citation, and will be given with the full publication.

(15) Sutton, P. W.; Dahl, L. F. *J. Am. Chem. Soc.* **1967**, *89*, 261.

structure of **3d** thereby confirms that both formerly doubly bonded units (vinylidene C=C ca. 130 pm,[10] ylide P=C ca. 170 pm[16]) have turned into singly bonded units upon formation of the new C–C bond, that the vinylidene ligand has turned into an alkylidyne ligand, and that the phosphorus ylide has turned into a phosphonium group. The structure, in accord with the electron-counting rules, thus implies the above-mentioned zwitterionic formulation. The complexes **3** are thereby homologous to the complexes $FeCo_2(CO)_9(\mu_3\text{-}\eta^1\text{-}CCH_2PR_3)$ which were obtained from **1** and PR_3.[11] They are also homologous to Shriver's complexes $[Fe_2Co(CO)_9(\mu_3\text{-}\eta^1\text{-}CPR_3)]^-$, which have yet another CH_2 group less between the trimetal unit and the phosphonium center.[17]

While C–C bond formation by combination of electrophilic and nucleophilic carbon centers is one of the most basic reactions in organic chemistry, it has, to our knowledge, never been performed in the way described here, namely, as an adduct formation between uncharged methylene units of nonpolar compounds. The reagents are either charged species like enolates or onium compounds or the primary adducts quickly undergo rearrangement reactions.[4,5] The ease of formation of the adducts **3** results from the fact that in the starting materials **1** and **2** the methylene units are in an unusual electronic situation due to their attachment to inorganic centers. Likewise the stability of the adducts rests on the efficient charge separation brought about by the cationic phosphonium group and the anionic $FeCo_2$ cluster unit at both ends of the CH_2–CHR chain. It therefore seems to us that the charge separation drives the C–C bond formation and not vice versa.

Acknowledgment. This work was supported by the Fonds der Chemischen Industrie and by the Stiftung Volkswagenwerk. We thank W. Deck for technical help.

Registry No. **1**, 85249-99-6; **2a**, 3487-44-3; **2b**, 3739-97-7; **2c**, 859-65-4; **2d**, 1099-45-2; **3a**, 126156-16-9; **3b**, 126156-17-0; **3c**, 126156-18-1; **3d**, 126156-19-2.

---

(16) Bart, J. C. J. *J. Chem. Soc. B* **1969**, 350.

(17) Ching, S.; Sabat, M.; Shriver, D. F. *Organometallics* **1989**, *8*, 1047.

Facile Synthesis and Structural Characterization of $[(Ph_2PCHCH_2)(\mu\text{-}\eta^3\text{-}Ph_2PCHCH_2)Pd^I]_2(BF_4)_2$: Unprecedented Formation of a Structurally Unusual Palladium(I) Complex

William L. Wilson and John H. Nelson*

Department of Chemistry, University of Nevada
Reno, Nevada 89557

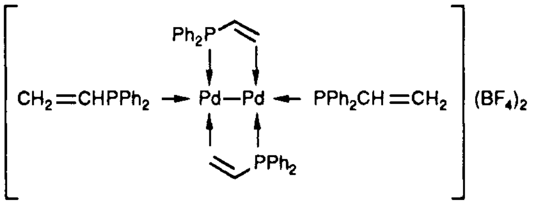
Nathaniel W. Alcock

Department of Chemistry, University of Warwick
Coventry CV47AL, England

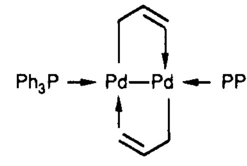
Received December 27, 1989

Summary: Photochemical reaction of $(Ph_2PCH{=}CH_2)_2PdCl_2$ with $AgBF_4$ produces the novel palladium(I) phosphaallyl complex $[(Ph_2PCH{=}CH_2)(\mu\text{-}\eta^3\text{-}Ph_2PCH{=}CH_2)Pd^I]_2(BF_4)_2$ in high yield. This compound is fluxional in solution.

In light of current interest[1] in the coordination chemistry of heteroatom compounds that are isolobal[2] with classical unsaturated hydrocarbon fragments, we wish to report the facile synthesis[3] of the novel compound [(vinyldiphenylphosphine)(μ-η^3-diphenylphosphaallyl)palladium(I)]$_2$(BF_4)$_2$, **1**. Compound **1** is the first example of a neutral vinylphosphine acting as a bridging μ-η^3 four-electron donor to two metals. As such it is a neutral phosphaallyl analogue of the Pd(I) compound[4] $[(Ph_3P)(\mu\text{-}\eta^3\text{-}C_3H_5)Pd^I]_2$, **2**, and of the anionic phosphaallyl compound[1] $(CO)_5W(\mu\text{-}\eta^3\text{-}PhPCH{=}CH_2)(C_5H_5)FeCO$, **3**. In **3** the anionic phosphaallyl moiety is a two-electron donor to W(0) and a three-electron donor to Fe(I). Alternatively, compound **1** could be considered to contain a bridging η^1-P, η^2-(C=C) vinylphosphine, but in light of the structural similarities of compounds **1** and **2** we prefer the μ-η^3-phosphaallyl bonding description.



1



2

Reaction of dichlorobis(vinyldiphenylphosphine)palladium(II)[5] with slightly more than 2 equiv of silver fluoroborate in dichloromethane in the presence of light produces **1**, which is isolated in 70% yield as a bright yellow crystalline compound after slow addition of diethyl ether to the filtered dichloromethane reaction mixture. The unexpected formation of **1** is yet another example of an unusual result[6] of an anticipated simple silver salt metathesis[7] of a noble-metal halide complex.

In contrast to the formation of **1**, similar reactions with $[PhP(C_2H_3)_2]_2MCl_2$, M = Pd[5] or Pt,[8] or $(Ph_2PC_2H_3)_2PtCl_2$[9]

---

(1) Mercier, F.; Fischer, J.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 357. Mercier, F.; Hugel-LeGoff, C.; Mathey, F. *Organometallics* **1988**, *7*, 955.

(2) Mathey, F. *Nouv. J. Chim.* **1987**, *11*, 585.

(3) Under a purge of N_2 gas, 2.14 g of $AgBF_4$ (0.0110 mol) was added to a solution of 3.0 g of $(Ph_2PCH{=}CH_2)_2PdCl_2$ (0.0050 mol) in 125 mL of CH_2Cl_2 in a 500-mL round-bottom flask. White AgCl precipitate began to form immediately. The flask was closed with a rubber septum and stirred with a magnetic stirrer under ambient light. During this time the precipitate became black and BF_3 gas was evolved. The gas was released periodically by using a hypodermic needle. After 1 week the reaction was complete as evidenced by cessation of gas evolution. The reaction mixture was gravity filtered, and the resulting bright yellow solution was reduced to an orange yellow solid by rotary evaporation. This solid was recrystallized by diffusion of diethyl ether into a saturated 3:1 CH_2Cl_2:Et_2O solution of the compound at −20 °C, yielding 2.12 g (0.00175 mol) of $[(Ph_2PCH{=}CH_2)(\mu\text{-}\eta^3\text{-}Ph_2PCH{=}CH_2)Pd^I]_2(BF_4)_2$ (70.0%) as yellow crystals, mp 204 °C. Anal. Calcd for $C_{56}H_{52}B_2F_8P_4Pd_2$: C, 58.04; H, 4.49; P, 10.69; Pd, 18.36. Found: C, 57.79; H, 4.52; P, 10.51; Pd, 18.20.

(4) Jolly, P. W.; Kruger, C.; Schick, K. P.; Wilke, G. *Z. Naturforsch., B: Anorg. Chem. Org. Chem.* **1980**, *35b*, 926.

(5) Rahn, J. A.; Holt, M. S.; O'Neil-Johnson, M.; Nelson, J. H. *Inorg. Chem.* **1988**, *27*, 1316.

(6) Liston, D. J.; Lee, Y. J.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1989**, *111*, 6643.

(7) Hartley, F. R.; Murray, S. G.; Wilkinson, A. *Inorg. Chem.* **1989**, *28*, 549.

(8) Holt, M. S.; Nelson, J. H.; Alcock, N. W. *Inorg. Chem.* **1986**, *25*, 2288.

(9) Rahn, J. A.; Holt, M. S.; Gray, G. A.; Alcock, N. W.; Nelson, J. H. *Inorg. Chem.* **1989**, *28*, 217.

0276-7333/90/2309-1699$02.50/0