2288 *Organometallics* **2001,** *20,* 2288−2293

η^1-Ligation versus Pnictogen−Carbon Double Bond Cleavage: The Contrasting Behavior of Phospha- and Arsaalkenes [$Tp^*(CO)_2M{\equiv}C{-}E{=}C(NMe_2)_2$] [E = P, As; M = Mo, W; $Tp^* = HB(3,5\text{-}Me_2pz)_3$] toward [$Au(CO)Cl$]

Lothar Weber,*,† Gottfried Dembeck,† Peter Lönneke,‡
Hans-Georg Stammler,† and Beate Neumann†

Fakultät für Chemie der Universität Bielefeld, Universitätsstrasse 25, D-33615 Bielefeld, Germany, and Institut für Anorganische Chemie der Universität Leipzig, Johannisallee 29, D-04103 Leipzig, Germany

Received January 29, 2001

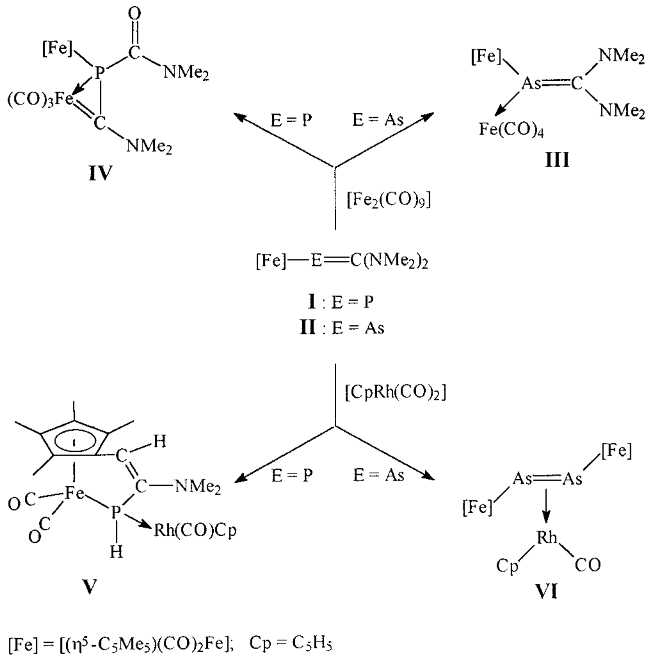
Reaction of [$Tp^*(CO)_2M{\equiv}C{-}P{=}C(NMe_2)_2$] [**1a**, M = Mo; **1b**, W; $Tp^* = HB(3,5\text{-}Me_2pz)_3$] with 2 molar equiv of [$Au(CO)Cl$] afforded the trinuclear complexes [$Tp^*(CO)_2M{\equiv}C{-}P(AuCl)_2C(NMe_2)_2$] **2a** (M = Mo) and **2b** (M = W). In marked contrast to this the arsenic analogues [$Tp^*(CO)_2M{\equiv}C{-}As{=}C(NMe_2)_2$] (**3a**, M = Mo; **3b**, M = W), when treated with the gold complex, give rise to As=C cleavage with formation of the gold carbene complex [$ClAuC(NMe_2)_2$] (**5**) and the functionalized cyclotriarsanes [$\{Tp^*(CO)_2M{\equiv}C{-}As\}_3$] **4a** (M = Mo) and **4b** (M = W). Compounds **2a**,**b** and **4a**,**b** have been characterized by IR and ^{1}H and ^{13}C NMR spectroscopy. In addition, the molecular structures of **2a**, **2b**, and **5** have been determined by single-crystal X-ray structural analyses.

Introduction

Phosphaalkenes[1] and arsaalkenes[2] with identical substitution patterns in many cases display similar chemical reactivities. There exist, however, a few remarkable exceptions from this rule of thumb.The reaction of arsaalkene [$Cp^*(CO)_2FeAs{=}C(NMe_2)_2$] (**II**) with an equimolar amount of [$Fe_2(CO)_9$] cleanly afforded the tetracarbonyliron adduct **III**,[3] whereas the phosphorus analogue [$Cp^*(CO)_2FeP{=}C(NMe_2)_2$] (**I**) was converted into the η^2-phosphinocarbene complex **IV**.[4] Compound **I** and [$CpRh(CO)_2$] underwent a condensation reaction with formation of complex **V**.[5] Under comparable reaction conditions arsaalkene **II** afforded the η^2-diferriodiarsene complex **VI**[5] (Scheme 1).

Carbon disulfide was inserted into the pnictogen−silicon bonds of metalloarsane [$Cp^*(CO)_2Fe{-}As(SiMe_3)_2$] to yield the stable ferrioarsaalkene **VII**.[6] The corresponding ferriophosphaalkene, however, readily extruded $(Me_3Si)_2S$, and the resulting species dimerized to give heterocycle **VIII**[6] (Scheme 2).

Scheme 1



[Fe] = [(η^5-C_5Me_5)(CO)$_2$Fe]; Cp = C_5H_5

Here we report on the reaction of the transition metal carbyne-functionalized phospha- and arsa-alkenes [$Tp^*(CO)_2M{\equiv}C{-}E{=}C(NMe_2)_2$] (E = P, As; M = Mo, W) toward carbonylgold chloride.

Experimental Section

All operations were performed under dry, oxygen-free dinitrogen using standard Schlenk techniques. Solvents were dried by standard methods and freshly distilled under nitrogen prior to use. Infrared spectra were recorded on a Bruker FT-IR IFS66 spectrometer. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded at 22 °C using a Bruker AC 100 (^{1}H, 100.13 MHz;

---

† Universität Bielefeld.

‡ Universität Leipzig.

[1] (a) Dillon, K. B.; Mathey, F.; Nixon, J. F. *Phosphorus: The Carbon Copy*; Wiley: Chichester, 1998, pp 88−127. (b) Weber, L. *Angew. Chem.* **1996**, *108*, 292; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 271, and references therein.

[2] *Review*: Weber, L. *Chem. Ber.* **1996**, *129*, 367, and references therein.

[3] Weber, L.; Scheffer, M. H.; Stammler, H.-G.; Neumann, B. *Eur. J. Inorg. Chem.* **1998**, 55.

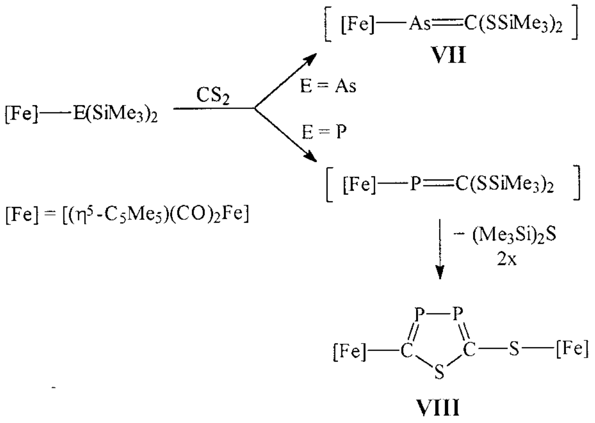
[4] Weber, L.; Kaminski, O.; Quasdorff, B.; Stammler, H.-G.; Neumann, B. *J. Organomet. Chem.* **1997**, *529*, 329.

[5] Weber, L.; Scheffer, M. H.; Stammler, H.-G.; Neumann, B. *Inorg. Chim. Acta* **1999**, *291*, 311.

[6] Weber, L.; Uthmann, S.; Torwiehe, B.; Kirchhoff, R.; Boese, R.; Bläser, D. *Organometallics* **1997**, *16*, 3188.

10.1021/om010071m CCC: $20.00

Scheme 2



^{31}P, 40.53 MHz) and a Bruker Avance DRX 500 (^{1}H, 500.13 MHz; ^{13}C, 125.75 MHz; ^{31}P, 202.46 MHz). Standards were $SiMe_4$ (^{1}H, ^{13}C) and 85% H_3PO_4 (^{31}P). Elemental analyses were performed at Mikroanalytisches Laboratorium H. Kolbe, Mülheim/Ruhr. The complexes $[Tp^*(CO)_2M{\equiv}C{-}P{=}C(NMe_2)_2]$ (M = Mo, W),[7] $[Tp^*(CO)_2M{\equiv}C{-}As{=}C(NMe_2)_2]$ (M = Mo, W),[8] and $[Au(CO)Cl]$[9] were synthesized according to literature procedures.

$[Tp^*(CO)_2Mo{\equiv}C{-}P(AuCl)_2C(NMe_2)_2]$ (2a). Under an atmosphere of CO a solution of 0.28 g (1.04 mmol) of $[Au(CO)Cl]$ in 20 mL of toluene was added dropwise to a chilled slurry (−78 °C) of 0.34 g (0.57 mmol) of $[Tp^*(CO)_2Mo{\equiv}C{-}P{=}C(NMe_2)_2]$ (**1a**) in 50 mL of toluene. After 1 h the slurry was allowed to warm to ambient temperature, whereupon all **1a** went into solution. After 24 h of stirring the color of the mixture had changed from red to dark violet. A black-violet precipitate was filtered off, and the filtrate was evaporated to dryness. The black residue was continuously extracted with *n*-pentane (30 mL, 2 h) and subsequently with diethyl ether (30 mL, 2 h). An amorphous orange solid remained in the extractor. This solid was suspended in 20 mL of CH_2Cl_2, stirred for 2 h, and filtered. The same procedure was repeated two times, and the combined filtrates were filtered through a pad (2 cm) of anhydrous Na_2SO_4. The filtrate was concentrated to ca. 10 mL and stored for 24 h at 5 °C to afford red crystals of **2a** (yield 0.44 g, 73%). IR (KBr): $\tilde{\nu}$ 2553 w (B−H), 2002 vs (CO), 1921 vs (CO) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 2.30 (s, 6H, Tp*CC*H*$_3$), 2.38 (s, 6H, Tp*CC*H*$_3$), 2.62 (s, 6H, Tp*CC*H*$_3$), 3.47 (s, 12H, NCH$_3$), 5.76 (s, 1H, Tp*C*H*), 5.93 (s, 2H, Tp*C*H*). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 12.9 (s, Tp*C*C*H$_3$), 14.7 (s, Tp*C*C*H$_3$), 17.0 (s, Tp*C*C*H$_3$), 46.9 (s, NCH$_3$), 106.7 (s, Tp**C*H), 107.6 (s, Tp**C*H), 145.8 (s, Tp**C*CH$_3$), 146.4 (s, Tp**C*CH$_3$), 151.5 (s, Tp**C*CH$_3$), 152.0 (s, Tp**C*CH$_3$), 181.7 (s, PCN$_2$), 226.1 (s, CO), 280.9 (s, Mo≡C). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 16.2 s. MS/MALDI-(DCTB): *m/z* 1001.5 (M$^+$ − 2CO). Anal. Calcd for $C_{23}H_{34}Au_2BCl_2MoN_8O_2P$ (1057.14): C, 26.13; H, 3.24; N, 10.60. Found: C, 25.71; H, 3.18; N, 10.15. Samples still contain impurities of CH_2Cl_2.

$[Tp^*(CO)_2W{\equiv}C{-}P(AuCl)_2C(NMe_2)_2]$ (2b). Analogously, a sample of $[Tp^*(CO)_2W{\equiv}C{-}P{=}C(NMe_2)_2]$ (**1b**) (0.36 g, 0.53 mmol) in 60 mL of toluene was combined with a solution of $[Au(CO)Cl]$ (0.28 g, 1.07 mmol) in 20 mL of toluene. The light orange powder obtained after extraction of the crude product with *n*-pentane and diethyl ether was dissolved in CH_2Cl_2 (30 mL) and filtered through a pad (ca 2 cm) of anhydrous Na_2SO_4. The blood-red filtrate was concentrated to ca. 10 mL and stored at 5 °C. After 48 h red microcrystalline **2b** was filtered off (0.48 g, 79%). IR (KBr): $\tilde{\nu}$ 2552 w (B−H), 1985 vs (CO), 1896 vs (CO) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 2.31 (s, 3H, Tp*CC*H*$_3$), 2.35 (s, 3H, Tp*CC*H*$_3$), 2.39 (s, 6H, Tp*CC*H*$_3$), 2.64 (s, 6H, Tp*CC*H*$_3$), 3.41 (s, 12H, NCH$_3$), 5.79 (s, 1H, Tp*C*H*), 5.97 (s, 2H, Tp*C*H*). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 12.8 (s, Tp*C*C*H$_3$), 15.3 (s, Tp*C*C*H$_3$), 17.5 (s, Tp*C*C*H$_3$), 46.1 (s, NCH$_3$), 106.9 (s, Tp**C*H), 107.1 (s, Tp**C*H), 145.7 (s, Tp**C*CH$_3$), 146.5 (s, Tp**C*CH$_3$), 152.5 (s, Tp**C*CH$_3$), 152.9 (s, Tp**C*CH$_3$), 185.4 (s, PCN$_2$), 225.1 (s, CO), 273.0 (s, W≡C). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 16.2 s. MS/MALDI(DCTB): *m/z* 912 (M$^+$ − AuCl). Anal. Calcd for $C_{23}H_{34}Au_2BCl_2N_8O_2PW$ (1145.05): C, 22.84; H, 2.91; N, 8.52. Found: C, 23.22; H, 3.04; N, 8.63.

Reaction of $[Tp^*(CO)_2Mo{\equiv}C{-}As{=}C(NMe_2)_2]$ (3a) with $[Au(CO)Cl]$. A chilled slurry (−78 °C) of **3a** (0.75 g, 1.18 mmol) in 80 mL of toluene was combined with a solution of $[Au(CO)Cl]$ (0.40 g, 1.54 mmol) in 20 mL of toluene under an atmosphere of CO for 1 h. Warming to room temperature was accompanied by the complete dissolution of **3a** and by a color change from red to dark violet. After 24 h of stirring the reaction mixture was concentrated to ca. 30 mL and stored for 24 h at −30 °C. Yellow crystalline $[(Me_2N)_2CAuCl]$ (0.30 g, 77%) was removed by filtration. The violet filtrate was evaporated to dryness. The violet solid residue was placed in an extractor and continuously extracted with 30 mL of boiling *n*-pentane (5 h) and subsequently with 30 mL of boiling diethyl ether (15 h). The ether extract was stored for 48 h at 5 °C to afford $[\{Tp^*(CO)_2Mo{\equiv}C{-}As\}_3]$ (**4a**) as red microcrystals (0.37 g, 59% yield).

4a: IR (KBr): $\tilde{\nu}$ 2527 w (B−H), 1987 vs (CO), 1909 vs (CO) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 2.13 (s, 6H, Tp*CC*H*$_3$), 2.19 (s, 6H, Tp*CC*H*$_3$), 2.26 (s, 6H, Tp*CC*H*$_3$), 2.29 (s, 6H, Tp*CC*H*$_3$), 2.33 (s, 12H, Tp*CC*H*$_3$), 2.35 (s, 6H, Tp*CC*H*$_3$), 2.36 (s, 6H, Tp*CC*H*$_3$), 2.57 (s, 6H, Tp*CC*H*$_3$), 5.39 (s, 2H, Tp*C*H*), 5.41 (s, 2H, Tp*C*H*), 5.73 (s, 3H, Tp*C*H*), 5.93 (s, 2H, Tp*C*H*). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 12.1 (s, Tp*C*C*H$_3$), 12.2 (s, Tp*C*C*H$_3$), 12.3 (s, Tp*C*C*H$_3$), 13.95 (s, Tp*C*C*H$_3$), 14.05 (s, Tp*C*C*H$_3$), 14.9 (s, Tp*C*C*H$_3$), 15.3 (s, Tp*C*C*H$_3$), 16.0 (s, Tp*C*C*H$_3$), 16.1 (s, Tp*C*C*H$_3$), 105.3 (s, Tp**C*H), 105.4 (s, Tp**C*H), 106.0 (s, Tp**C*H), 143.9 (s, Tp**C*CH$_3$), 144.0 (s, Tp**C*CH$_3$), 144.9 (s, Tp**C*CH$_3$), 145.2 (s, Tp**C*CH$_3$), 145.5 (s, Tp**C*CH$_3$), 150.9 (s, Tp**C*CH$_3$), 151.3 (s, Tp**C*CH$_3$), 225.8 (s, CO), 226.4 (s, CO), 226.8 (s, CO), 304.8 (s, 2C, Mo≡C), 310.6 (s, 1C, Mo≡C). Anal. Calcd for $C_{54}H_{66}As_3B_3Mo_3N_{18}O_6$ (1608.27): C, 40.33; H, 4.14; N, 15.68. Found: C, 41.02; H, 4.25; N, 15.20. According to ^{1}H NMR the compound crystallized with 0.6 molar equiv of diethyl ether. Anal Calcd for $C_{54}H_{66}As_3B_3Mo_3N_{18}O_6{\cdot}0.6C_4H_{10}O$ (1652.67): C, 40.99; H, 4.39; N, 15.25.

5: ^{1}H NMR (CD_2Cl_2): δ 3.25 (s, NCH$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 45.3 (s, NCH$_3$), 203.5 (s, AuC). Lit.:[10] ^{13}C{^{1}H} NMR (DMSO-d_6): δ 44.5, 200.0.

Reaction of $[Tp^*(CO)_2W{\equiv}C{-}As{=}C(NMe_2)_2]$ (3b) with $[Au(CO)Cl]$. Analogously, a sample of **3b** (0.65 g, 0.90 mmol) was reacted with 0.36 g (1.38 mmol) of $[Au(CO)Cl]$ in 100 mL of toluene. Concentration of the resulting reaction mixture to ca. 30 mL and storage at −30 °C for 24 h yielded 0.22 g (73%) of yellow crystalline $[(Me_2N)_2CAuCl]$ (**5**). The mother liquor was freed from solvent and volatiles, and the solid dark violet residue was extracted with *n*-pentane and then with diethyl ether as described before. The ethereal extract was stored for 48 h at 5 °C to yield 0.36 g (64%) of blood-red microcrystalline $[\{Tp^*(CO)_2W{\equiv}C{-}As\}_3]$ (**4b**).

4b: IR (KBr): $\tilde{\nu}$ 2546 w (B−H), 1972 vs (CO), 1887 vs (CO) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 2.13 (s, 6H, Tp*CC*H*$_3$), 2.20 (s, 6H, Tp*CC*H*$_3$), 2.27 (s, 6H, Tp*CC*H*$_3$), 2.29 (s, 6H, Tp*CC*H*$_3$), 2.33 (s, 12H, Tp*CC*H*$_3$), 2.36 (s, 6H, Tp*CC*H*$_3$), 2.38 (s, 6H, Tp*CC*H*$_3$), 2.58 (s, 6H, Tp*CC*H*$_3$), 5.42 (s, 2H, Tp*C*H*), 5.43 (s, 2H, Tp*C*H*), 5.75 (s, 3H, Tp*C*H*), 5.96 (s, 2H, Tp*C*H*). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 12.65 (s, Tp*C*C*H$_3$), 12.7 (s, Tp*C*C*H$_3$),

---

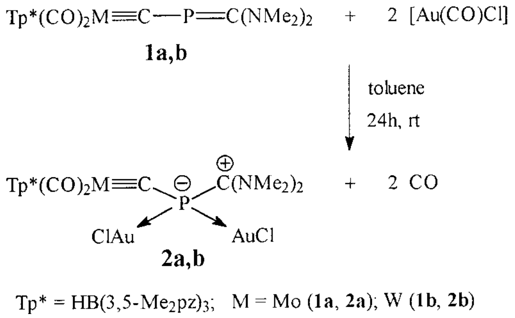
(7) Weber, L.; Dembeck, G.; Boese, R.; Bläser, D. *Chem. Ber./Recl.* **1997**, *130*, 1305.

(8) Weber, L.; Dembeck, G.; Boese, R.; Bläser, D. *Organometallics* **1999**, *18*, 4603.

(9) *Handbuch der Präparativen Chemie*; Brauer, G.. Ed.; Enke: Stuttgart, 1981; p 1965.

(10) Fehlhammer, W. P.; Finck, W. *J. Organomet. Chem.* **1991**, *414*, 261.

Scheme 3



12.8 (s, Tp*C*C*H$_3$), 15.2 (s, Tp*C*C*H$_3$), 15.25 (s, Tp*C*C*H$_3$), 15.5 (s, Tp*C*C*H$_3$), 16.6 (s, Tp*C*C*H$_3$), 17.4 (s, Tp*C*C*H$_3$), 17.6 (s, Tp*C*C*H$_3$), 106.1 (s, Tp**C*H), 106.2 (s, Tp**C*H), 106.8 (s, Tp**C*H), 144.4 (s, Tp**C*CH$_3$), 144.6 (s, Tp**C*CH$_3$), 145.4 (s, Tp**C*CH$_3$), 145.8 (s, Tp**C*CH$_3$), 146.1 (s, Tp**C*CH$_3$), 152.3 (s, Tp**C*CH$_3$), 152.9 (s, Tp**C*CH$_3$), 224.5 (s, CO), 225.4 (s, CO), 291.5 (s, 2C, W≡C), 296.0 (s, 1C, W≡C). Anal. Calcd for $C_{54}H_{66}As_3B_3N_{18}O_6W_3$ (1872.00): C, 34.65; H, 3.55; N, 13.47. Found: C, 34.80; H, 3.89; N, 13.10.

Results and Discussion

Reaction of the phosphaalkenyl-functionalized carbyne complexes **1a** and **1b** with 2 molar equiv of carbonylgold chloride in toluene at ambient temperature led to a color change from red to dark violet within 24 h. Crude products were obtained from the solution by removal of solvent and volatiles in vacuo and by repeated extraction of the residue with *n*-pentane and diethyl ether. Purification was effected by crystallization from CH_2Cl_2 at 5 °C to afford the red microcrystalline gold complexes [Tp*(CO)$_2$M≡C−P(AuCl)$_2$C(NMe$_2$)$_2$] (**2a**, M = Mo; **2b**, M = W) (Scheme 3). The IR spectra of **2a** and **2b** are dominated by two intense ν(CO) bands at $\tilde{\nu}$ 2002, 1921 cm^{-1} (**2a**) and $\tilde{\nu}$ 1985, 1896 cm^{-1} (**2b**). Thus, the ligation of **1a** ($\tilde{\nu}$ 1946, 1846 cm^{-1}) and **1b** ($\tilde{\nu}$ 1935, 1848 cm^{-1}) by two [AuCl] fragments via the phosphorus atom exerts a significant electron withdrawal from the [M(CO)$_2$] fragments. A similar observation was made recently by the methylation of **1a** and **1b**. In [Tp*(CO)$_2$M≡C(Me)C(NMe$_2$)$_2$]$^+$ two intense ν(CO) bands were recorded at 1997 and 1915 cm^{-1} (M = Mo) or 1982 and 1893 cm^{-1} (M = W).[11]

Compared to the starting materials (**1a**, δ 62.3; **1b**, δ 49.0), the ^{31}P NMR resonances of products **2a** and **2b** (δ 16.2) are markedly shielded. A tungsten−phosphorus coupling as it is present in **1b** (J = 51.4 Hz) cannot be detected in **2b**. In [Tp*(CO)$_2$M≡C−P(Me)CNMe$_2$)$_2$]$^+$ similar ^{31}P NMR shifts were observed [δ 18.3 (M = Mo) and 17.2 (M = W)].

Strong high-field shifts were also observed for the ^{13}C nuclei of the carbyne ligand on going from **1a** (δ 337.5 d, $^1J_{PC}$ = 111.3 Hz) or **1b** (δ 318.3 d, $^1J_{PC}$ = 101.2 Hz) to **2a** (δ 280.9 s) and **2b** (δ 273.0 s). The ^{13}C NMR resonances of the tricoordinate carbon atom of the bisaminocarbenium unit in **2a** (δ 181.7 s) and **2b** (δ 185.4 s) were shielded to a much lesser extent when compared with the starting materials **1a** (δ 202.7 d, $^1J_{PC}$ = 89.0 Hz) and **1b** (δ 201.3 d, $^1J_{PC}$ = 88.3 Hz). Like in the case of the carbyne carbon atom, no PC coupling was observed in the spectra of the products.

In the cations [Tp*(CO)$_2$M≡C−P(Me)C(NMe$_2$)$_2$]$^+$ the ^{13}C nuclei of the carbyne ligand and the bisaminocarbenium unit gave rise to doublet resonances at δ 287.68 (d, $^1J_{PC}$ = 94.2 Hz, M = Mo) or δ 273.04 (d, $^1J_{PC}$ = 83.0 Hz, M = W) and δ 177.65 (d, $^1J_{PC}$ = 45.9 Hz, M = Mo) or δ 178.25 (d, $^1J_{PC}$ = 45.9 Hz). The electron-draft from the organometallic ligand onto the two gold centers is also mirrored in high-field shifts of the carbonyls (**1a**, 229.5 s; **2a**, 226.1; **1b**, 228.1; **2b**, 225.1). These chemical shifts of **2a** and **2b** are nearly identical with those of the carbonyls in the cations [Tp*(CO)$_2$M≡C−P(Me)C(NMe$_2$)$_2$]$^+$ (M = Mo, δ 226.93; W, 225.48).

Under comparable conditions the reaction between the arsaalkenyl-functionalized carbyne complexes **3a** and **3b** with carbonylgold chloride in toluene took a completely different course. From the dark violet reaction solution after concentration and storage at −30 °C carbene complex [(Me$_2$N)$_2$CAuCl] (**5**) was isolated as yellow crystals in ca. 70% yield. The violet mother liquor was worked up analogously, and from the ethereal extracts the cyclotriarsanes **4a** and **4b** were separated as red microcrystalline solids in yields of 59% (**4a**) and 64% (**4b**), respectively (Scheme 4). The gold carbene complex **5**, which was previously prepared by treatment of [1,2-(ClAuCN)$_2$C$_6$H$_4$] with dimethylamine,[10] was identified by elemental analyses and NMR data (^{1}H, ^{13}C). In addition an X-ray diffraction study of **5** has proven the identity of the compound.

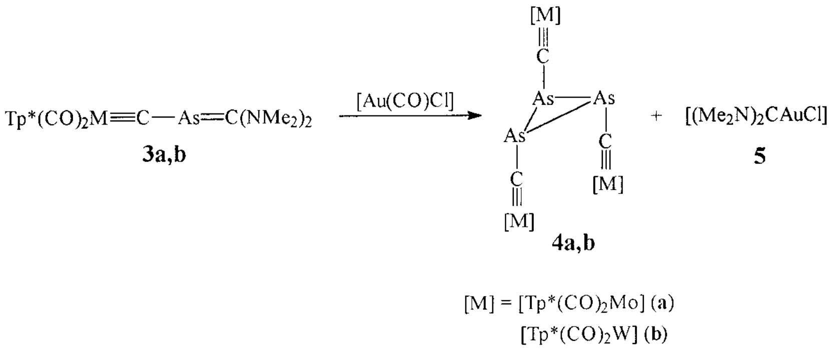
The absence of protons of the methylamino group in the ^{1}H NMR spectra of **4a** and **4b** gave first evidence that the products are oligomers of the hypothetical arsanediyls [Tp*(CO)$_2$M≡C−As] (M = Mo, W). The ^{13}C{^{1}H} NMR spectra of **4a** and **4b** are particularly informative in the low-field region, where two singlets in the ratio 2:1 at δ 304.8 and 310.6 (M = Mo) or δ 291.5 and 296.0 (M = W) appeared for the metal-bound carbon atoms of the novel organoarsenic ligand. This observation agrees with the presence of a cyclotriarsane ring with two metal−carbyne substituents in cis-disposition and the remaining one on the opposite face of the ring. In comparison to the starting materials **3a** (δ 349.7) and **3b** (δ 329.1), these resonances are strongly shielded. The ^{13}C nuclei of the carbonyls in **4a** and **4b** give rise to singlets at δ 225.8, 226.4, and 226.8 (M = Mo) or δ 224.5 and 225.4 (M = W), respectively. The shielding of these signals relative to **3a** (δ 229.1) and **3b** (δ 227.6) points to a decreased σ-donor/π-acceptor capacity of the cyclotriarsane−triscarbyne ligand in comparison to the organoarsenic ligand in the precursor molecules. In keeping with this, the bands of the carbonyl stretching vibrations of **3a** (ν 1947, 1863 cm^{-1}) and **3b** (ν 1936, 1848 cm^{-1}) are hypsochromically shifted in the products **4a** (ν 1987, 1909 cm^{-1}) and **4b** (ν 1972, 1887 cm^{-1}).

X-ray Structural Analyses of 2a and 2b. The crystal and molecular structures of the gold complexes **2a** and **2b** have been determined by X-ray diffraction studies (see Figure 1, Tables 1 and 2). Both compounds crystallize with three molecules of CH_2Cl_2 in the monoclinic space group $P2_1/c$. Their bonding parameters are identical within the 3-fold standard deviation, and therefore the decription of the structure is confined to

---

[11] Weber, L.; Dembeck, G.; Stammler, H.-G.; Neumann, B.; Schmidtmann, M.; Müller, A. *Organometallics* **1998**, *17*, 5254.

Scheme 4



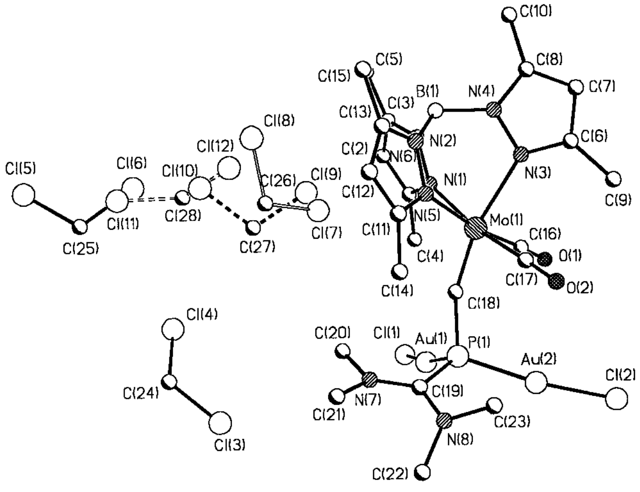


Figure 1. Molecular structure of **2a**·3CH$_2$Cl$_2$ in the crystal.

the molydenum derivative **2a**. The complex is a monomeric molecule with distorted octahedral geometry. Three facial positions are occupied by the nitrogen atoms of the tripodal ligand. The Mo(1)−N(3) bond length of 2.2912(15) Å is significantly longer than the remaining Mo−N bonds [2.2155(15) and 2.2067(15) Å], which reflects the pronounced trans-influence of the carbyne ligand. The bond angles between the organophosphorus ligand and the two carbonyl ligands [81.29(7)° and 82.40(7)°] are smaller than in [Tp*(CO)$_2$W≡C−P=C(NEt$_2$)$_2$] (**1c**) [85.5(3)° and 88.1(3)°]. Accordingly, the angles between the carbyne carbon atom C(18) and the nitrogen atoms N(1) and N(2) are more obtuse [106.76(7)°] than in **1c** [97.9(2)° and 100.2(2)°]. In contrast to **1c** [N−W−C = 178.8(2)°] the angle N(3)−Mo(1)−C(18) of 166.21(7)° deviates stronger from linearity. The most interesting structural feature of the molecule is the geometry of the organophosphorus fragment. The molybdenum−carbon bond Mo(1)−C(18) [1.8193(16) Å] is definitely a triple bond and compares well with the Mo≡C distances in [Tp*(CO)$_2$Mo≡C−Fe(CO)$_2$Cp] [1.819(6) Å][12] or [Tp*(CO)$_2$Mo≡CS(4-C$_6$H$_4$-NO$_2$)] [1.801(4) Å].[13] The valence angle at the sp-hybridized carbon atom Mo(1)−C(18)−P(1) of 160.56(11)° is more compressed than the corresponding angle WCP in **1c** [167.9(4)°]. In **1c** the bonds between the two-coordinate phosphorus atom and the two adjacent carbon atoms are of equal length [1.759(7) Å]. Ligation of two [AuCl] fragments at the tetracoordinate phosphorus atom in **2a** leads to an elongation of the former PC double bond P(1)−C(19) to a single bond of 1.8751(17) Å, whereas the other PC bond P(1)−C(18) is only slightly lengthened to 1.7842(16) Å. Atom C(19) has maintained its trigonal-planar environment (sum of angles 359.9°). Accordingly, the carbon−nitrogen bond lengths N(7)−C(19) [1.321(2) Å] and N(8)−C(19) [1.346(2) Å] are shortened in comparison to the calculated value of a Csp^2−Nsp^2 single bond of 1.450 Å.[14] The coordination sphere of the phosphorus atom is completed by two dicoordinate gold atoms, which are linked via Au−P single bonds of 2.2465(4) and 2.2517(4) Å. They are well comparable with the Au−P distances observed in the cation [{(Ph$_3$P)Au}$_6$C]$^{2+}$ [2.269(1)−2.274(1) Å][15] or in [(*t*Bu$_3$P)AuCl] [2.253(6) Å].[16] Unlike in [(*t*Bu$_3$P)AuCl][16] or [Au(CO)Cl],[17] where the gold atoms are linearly coordinated in **2a**, P−Au−Cl angles of 168.32(2)° and 169.88(2)° are observed. The gold−chlorine distances in **2a** [2.299(5) and 2.3079(4) Å] resemble those of [(*t*Bu$_3$P)AuCl] [2.284(6) Å] or [Au(CO)Cl] [2.261(6) Å]. An interesting question addresses bonding Au−Au interactions in polynuclear gold complexes. In the bisylide complex **6**[10] a transannular Au−Au distance of 3.023(1) Å was interpreted as a weak bonding interaction.[18] In a number of structures of gold compounds featuring pairs, rings, chains, or layers interatomic distances of 3.00 ± 0.25 are determined. The upper end of 3.25 Å reflects only weak bonding, whereas the lower end of 2.75 Å agrees with true metal−metal bonds.[19] In **2a** intramolecular and intermolecular Au−Au distances are nearly identical (3.582 and 3.592 Å) and exclude such weak bonding interactions. They are comparable with the Au−Au distances in the phosphonium ion [{(*t*Bu$_3$P)Au}$_4$P]$^+$, where they range from 3.4395(5) to 4.3314(5) Å.[20] The mode of coordination where an acyclic phosphaalkene functions as a (η^1-μ_2) 4e-donor is very rare and, to the best of our knowledge,

---

(12) Etienne, M.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1991**, *113*, 2324.

(13) Desmond, T.; Lalor, F. J.; Ferguson, G.; Parvez, M. *J. Chem. Soc., Chem. Commun.* **1984**, 75.

(14) Chernega, A. N.; Ruban, A. V.; Romanenko, V. D.; Markovskii, L. N.; Korkin, A. A.; Antipin, M. Y.; Struchkov, Y. T. *Heteroat. Chem.* **1991**, *2*, 229.

(15) Gabbai, F. P.; Schier, A.; Riede, J.; Schmidbaur, H. *Chem. Ber./Recl.* **1997**, *130*, 111.

(16) Schmidbaur, H.; Brachthäuser, B.; Steigelmann, O.; Beruda, H. *Chem. Ber.* **1992**, *125*, 2705.

(17) Jones, P. G. *Z. Naturforsch.* **1982**, *37b*, 823.

(18) Schmidbaur, H.; Mandl, E. J.; Richter, W.; Bejenke, V.; Frank, A.; Huttner, G. *Chem. Ber.* **1977**, *110*, 2236.

(19) Schmidbaur, H. *Gold Bull.* **1990**, *23*, 1.

(20) Zeller, E.; Beruda, H.; Schmidbaur, H. *Chem. Ber.* **1993**, *126*, 2033.

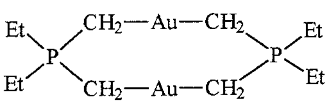
Table 1. Crystal Data and Structure Refinement for 2a, 2b, and 5

	2a	2b	5
formula	$C_{22}H_{36}Au_2BCl_2MoN_8O_2P\cdot 3CH_2Cl_2$	$C_{26}H_{36}Au_2BCl_2N_8O_2PW\cdot 3CH_2Cl_2$	$C_5H_{12}AuClN$
fw	1311.91	1398.81	332.58
T/K	100	296	100
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
a/Å	20.45700(10)	20.498(3)	9.2130(2)
b/Å	13.97100(10)	14.047(2)	9.3130(2)
c/Å	14.49500(10)	14.729(2)	9.8460(2)
β/deg	91.3280(2)	90.859(3)	93.3050(11)
V/Å^3	4141.63(5)	4240.4(12)	843.39(3)
Z	4	4	4
ρ_{calcd}/g cm^{-3}	2.104	2.191	2.619
μ/mm^{-1}	7.957	10.186	17.682
cryst size/mm^3	0.23 × 0.18 × 0.18	0.1 × 0.1 × 0.2	0.28 × 0.25 × 0.20
no. of reflns collected	33 983	23 973	2842
no. of data/params	17303/476	8343/442	1471/87
R1 [$I > 2\sigma(I)$]	0.0196	0.0550	0.0122
*w*R2 (all data)	0.0431	0.1643	0.0294
remarks	disorder of two CH_2Cl_2 on four positions (88:87:17:8)		

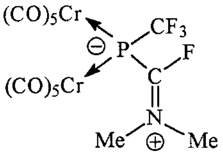
Table 2. Selected Bond Lengths (Å) and Angles (deg) of 2a

Mo(1)−C(16)	2.0068(19)	P(1)−C(19)	1.8751(17)
Mo(1)−C(17)	2.0039(19)	Au(1)−P(1)	2.2517(4)
Mo(1)−C(18)	1.8193(16)	Au(2)−P(1)	2.2465(4)
Mo(1)−N(1)	2.2155(15)	Au(1)−Cl(1)	2.3079(4)
Mo(1)−N(3)	2.2912(15)	Au(2)−Cl(2)	2.299(5)
Mo(1)−N(5)	2.2067(15)	C(19)−N(7)	1.321(2)
P(1)−C(18)	1.7842(16)	C(19)−N(8)	1.346(2)
Au(1)···Au(2)	3.582		
C(16)−Mo(1)−C(18)	81.29(7)	N(1)−Mo(1)−N(3)	83.75(6)
C(17)−Mo(1)−C(18)	82.40(7)	N(1)−Mo(1)−N(5)	81.93(6)
C(16)−Mo(1)−C(17)	88.11(8)	N(1)−Mo(1)−C(16)	93.82(7)
C(18)−Mo(1)−N(1)	106.76(7)	N(3)−Mo(1)−C(16)	89.25(7)
C(18)−Mo(1)−N(3)	166.21(7)	N(3)−Mo(1)−C(17)	87.31(6)
C(18)−Mo(1)−N(5)	106.76(6)	N(3)−Mo(1)−N(5)	83.19(6)
Mo(1)−C(18)−P(1)	160.56(11)	N(5)−Mo(1)−C(17)	94.99(5)
C(18)−P(1)−C(19)	102.94(7)	Au(1)−P(1)−Au(2)	105.56(2)
C(18)−P(1)−Au(1)	106.70(6)	Au(1)−P(1)−C(19)	114.29(5)
C(18)−P(1)−Au(2)	111.31(6)	Au(2)−P(1)−C(19)	115.81(5)
P(1)−C(19)−N(7)	121.20(13)	P(1)−C(19)−N(8)	117.34(12)
P(1)−Au(1)−Cl(1)	168.32(2)	P(1)−Au(2)−Cl(2)	169.88(2)
N(7)−C(19)−N(8)	121.40(16)		

restricted to the dinuclear complex **7**.[21]



6



7

A prerequisite for this type of coordination is obviously an inverse distribution of π-electron density $P^{\delta-}{=}C^{\delta+}$ in the phosphaalkene ligand.[22]

X-ray Structural Analysis of 4a. Very small single crystals of **4a** were grown from diethyl ether at −30 °C. Unfortunately, they were not suitable for a molecular structure analysis with satisfactory *R*-values. The topology of the molecule, however, was determined unambigiously as a cyclotriarsane with two $[Tp^*(CO)_2M{\equiv}C]$ substituents in cis-disposition at the arsenic atoms As(1) and As(2) and the third $[Tp^*(CO)_2M{\equiv}C]$ unit at As(3) at the opposite face of the ring.

Cyclotriarsanes are rare compounds and, to date, confined to $(As\textit{t}Bu)_3$[23] and $(Fc\text{-}As)_3$[24] (Fc = ferrocenyl). The facile metal-assisted cleavage of a As=C double bond of arsaalkenes has previously been reported for the reaction of $[Cp^*(CO)_2FeAs{=}C(NMe_2)_2]$ (**II**) with $[CpRh(CO)_2]$.[5] In this case two arsanediyl fragments were combined to an η^2-diarsene ligand.

Here, obviously, a cyclotrimerization of the arsanediyls $[Tp^*(CO)_2M{\equiv}C{-}As]$ (M = Mo, W) occurred. It is conceivable that this process was initiated by π-complex formation, cleavage of the endocyclic As−C bond by means of a second molecule of [Au(CO)Cl] to afford a dinuclear arsanediyl(carbene) complex, which eventually liberates the gold carbene complex and a transient arsanediyl species. The latter trimerizes to the cyclotriarsene (Scheme 5). Other mechanisms cannot be excluded today.

The process to some extent mirrors the synthesis of bis(carbene) complexes by reaction of electron-rich olefines with suitable transition metal complexes (cf. $(Ph_3P)AuCl/NaBF_4$).[25] The increased reactivity of the arsaalkene **3** with respect to the phosphaalkene **1** may be due to a decreased HOMO/LUMO energy gap in the former case. On the other hand, the decreased π-bond energy (38.2 kcal/mol in $HAs{=}CH_2$ versus 44.2 kcal/mol in $HP{=}CH_2$) may also contribute to the observed differences in the chemical behavior of **1** and **3** toward [Au(CO)Cl].[2]

X-ray Structural Analysis of 5. Single crystals of **5** were grown from toluene at −30 °C. The compound crystallizes in the monoclinic space group $P2_1/n$ (Tables 1, 3). The complex is monomeric, and the coordination of the gold atom is close to linear [C(1)−Au(1)−Cl(1) = 177.05(7)°] (Figure 2). In the related gold carbene complex [{Ph(Me$_2$N)C}AuCl](**8**),[26] the benzimidazol-2-ylidene complex **9**,[27] and the imidazolin-2-ylidene derivative **10**[28] the angles at the Au atoms were deter-

---

[21] Grobe, J.; Le Van, D.; Krebs, B.; Fröhlich, R.; Schiemann, A. *J. Organomet. Chem.* **1990**, *389*, C29.

[22] Review: Weber, L. *Eur. J. Inorg. Chem.* **2000**, 2425.

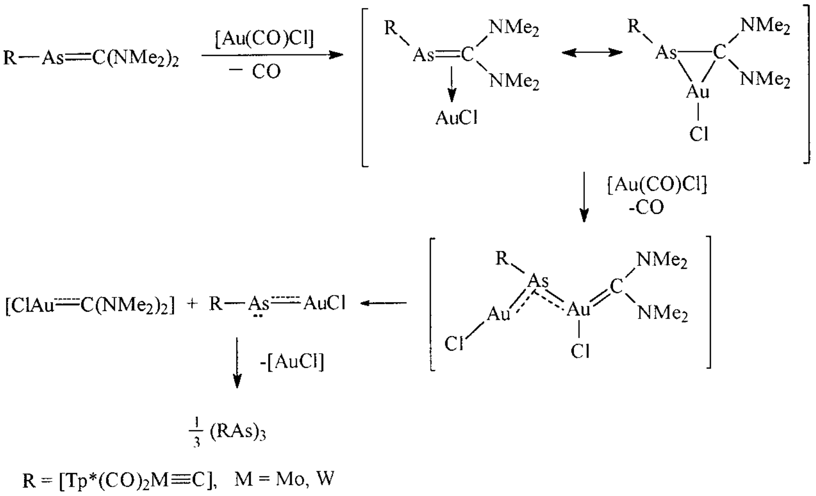
[23] (a) Baudler, M.; Bachmann, P. *Angew. Chem.* **1981**, *93*, 112; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 123. (b) Gleiter, R.; Schaefer, W.; Baudler, M. *J. Am. Chem. Soc.* **1985**, *107*, 8043.

[24] Spang, C.; Edelmann, F. T.; Noltemeyer, M.; Roesky, H. W. *Chem. Ber.* **1989**, 1247.

[25] Cetinkaya, B.; Dixneuf, P.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1974**, 827.

[26] Schubert, U.; Ackermann, K.; Aumann, R. *Cryst. Struct. Commun.* **1982**, *11*, 591.

Scheme 5



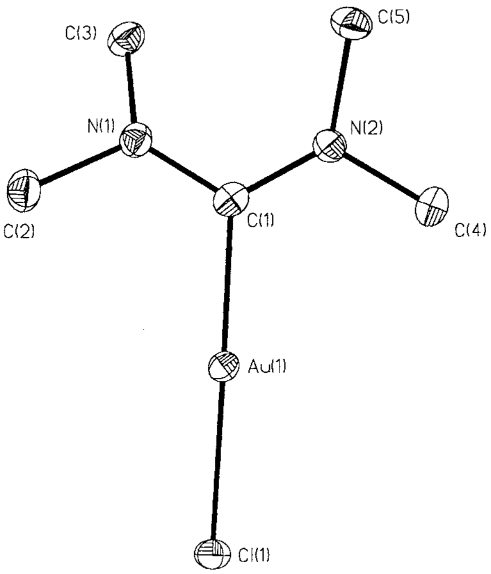


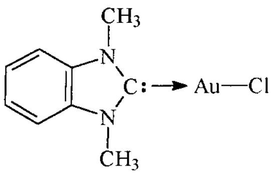
Figure 2. Molecular structure of **5** in the crystal.

Table 3. Selected Bond Lengths (Å) and Angles (deg) of 5

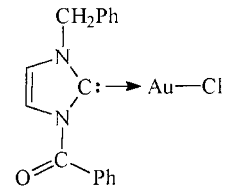
Au(1)–C(1)	2.009(3)	Au(1)–Cl(1)	2.3042(7)
N(1)–C(1)	1.342(4)	N(1)–C(2)	1.467(4)
N(2)–C(1)	1.336(4)	N(2)–C(4)	1.468(4)
N(2)–C(5)	1.471(4)	N(1)–C(3)	1.471(4)
C(1)–Au(1)–Cl(1)	177.05(7)	C(1)–N(1)–C(2)	120.7(3)
C(1)–N(1)–C(3)	124.9(3)	C(2)–N(1)–C(3)	112.7(2)
C(1)–N(2)–C(4)	121.0(2)	C(1)–N(2)–C(5)	125.5(2)
C(4)–N(2)–C(5)	112.9(2)	N(2)–C(1)–N(1)	119.3(3)
N(2)–C(1)–Au(1)	121.02(19)	N(1)–C(1)–Au(1)	119.7(2)

mined as 176.2(11)°, 178.1(3)°, and 176.8(3)°, respectively. The Au–C(1) distance is 2.009(3) Å and, within experimental error, is comparable to that reported[26–31] for [Au(carbene)Cl] and $[Au(carbene)_2]^+$ [1.97(1)–2.02(3) Å].

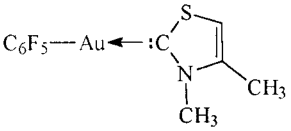
In the thiazol-2-ylidene complex **11** the gold–carbene carbon distance is 1.961(9) Å and only slightly shorter than the gold–aryl carbon bond of 1.993(10) Å.[32] The trigonal planar nitrogen atoms N(1) [sum of angles 358.3°] and N(2) [359.4°] in **5** are forming multiple bonds with the carbene carbon atom of 1.342(4) and 1.336(4) Å. Like in other transition metal compounds with imidazolin-2-ylidene ligands, metal to carbon π-back-bonding seems to be only of minor importance.[33] The gold–chlorine separation in **5** [2.3042(7) Å] and **9** [2.295(10) Å] is comparable with the Au–Cl bond lengths measured in **2a** and **2b**.



9



10



11

Acknowledgment. The present work was financially supported by the Deutsche Forschungsgemeinschaft (Bonn, Germany) and the Fonds der Chemischen Industrie (Frankfurt/M., Germany), which is gratefully acknowledged. We are grateful to Professor E. Hey-Hawkins, Universität Leipzig, for X-ray investigations in her department.

Supporting Information Available: Table of X-ray data, atomic coordinates, thermal parameters, and complete bond distances and angles and thermal ellipsoid plots for compounds **2a**,**b**, **4a**, **5** and the ^1H NMR spectra of **4a**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010071M

---

(27) Wang, H. M. J.; Chen, C. Y. L.; Lin, I. J. B. *Organometallics* **1999**, *18*, 1216.

(28) Bovio, B.; Burini, A.; Pietroni, B. R. *J. Organomet. Chem.* **1993**, *452*, 287.

(29) Bonati, F.; Burini, A.; Pietroni, B. R.; Bovio, B. *J. Organomet. Chem.* **1991**, *408*, 271.

(30) Britten, J. F.; Lock, C. J. L.; Wang, Z. *Acta Crystallogr.* **1992**, *C48*, 1600.

(31) Krüger, G. J.; Olivier, P. J.; Lindeque, L.; Raubenheimer, H. G. *Acta Crystallogr.* **1995**, *C51*, 1814.

(32) Raubenheimer, H. G.; Scott, F.; Roos, M.; Otte, R. *J. Chem. Soc., Chem. Commun.* **1990**, 1722.

(33) Herrmann, W. A.; Köcher, C.; Goossen, L. J.; Artus, G. R. J. *Chem. Eur. J.* **1996**, *2*, 1627.