Synthesis of Semibridging μ-Vinylidene Titanium−Copper and −Gold Complexes. Crystal and Molecular Structure of Cp*$_2$Ti(Cl)(μ-C=CH$_2$)AuPPh$_3$

Rüdiger Beckhaus,* Jürgen Oster, and Ruimin Wang

Department of Inorganic Chemistry, Technical University Aachen, Professor-Pirlet-Strasse 1, D-52056 Aachen, Germany

Uwe Böhme

Department of Inorganic Chemistry, Technical University Bergakademie Freiberg, Leipziger Strasse, D-09596 Freiberg, Germany

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The titanocene−vinylidene intermediate [Cp*$_2$Ti=C=CH$_2$] (**1**; Cp* = C$_5$(CH$_3$)$_5$), formed by methane elimination from Cp*$_2$Ti(CH=CH$_2$)(CH$_3$) (**2**), reacts with group 12 LM′X complexes ([Me$_3$PCuCl]$_4$ (**4a**), [Ph$_3$PCuCl]$_4$ (**4b**), [*i*-Pr$_3$PCuCl]$_4$ (**4c**), [Me$_3$PCuC≡CPh]$_4$ (**4d**), [Ph$_3$PAuCl] (**4e**) (Ti:M′ = 1:1)) to give heterodinuclear μ-vinylidene compounds Cp*$_2$Ti(X)(μ-C=CH$_2$)M′L (**5a**−**e**). The molecular structure of **5e** was determined by X-ray diffraction analysis, which revealed a titanium−gold bond asymmetrically bridged by the vinylidene ligand. A semibridging bonding mode for the C=CH$_2$ group in the new complexes is indicated by NMR spectroscopic and X-ray diffraction data.

Introduction

In the course of our investigations concerning the vinylidene intermediate [Cp*$_2$Ti=C=CH$_2$] (**1**),[1,2] which is conveniently generated by methane or ethylene elimination from Cp*$_2$Ti(CH=CH$_2$)CH$_3$ (**2**)[3] and Cp*$_2$-$\overline{\text{TiCH}_2\text{CH}_2\text{C}}$=CH$_2$ (**3**), we were interested in the possible formation of heterobinuclear vinylidene-bridged complexes starting from the mononuclear vinylidene species **1**. The only previously known μ-vinylidene complex containing titanium was obtained in a rearrangement reaction from Cp$_2$Ti(C≡CR)$_2$·CuX "tweezer" derivatives.[4] The stabilization of **1** by using donating ligands or donor-functionalized Cp groups has not been successful.[5] Dimerization of **1**, which is known for the methylene complex [Cp$_2$Ti=CH$_2$],[6] to form the bis(μ-vinylidene) [Cp*$_2$Ti(μ-C=CH$_2$)]$_2$ was not observed.

Considering the similarity of vinylidene, :C=CH$_2$, to the isoelectronic π-acceptor ligands carbon monoxide and carbon monosulfide,[7] the bonding modes **A-C** (Chart 1) may be expected for bridging vinylidene complexes. CO, CS, and C=CH$_2$ binuclear complexes are commonly found to be of the σ,σ-bridging type **A** (X = O,[8] S,[9] CH$_2$[10]). However, examples of the *side-on* bridging type **C**, involving donation from the filled π-orbitals of the C=X ligand into an empty orbital on M′, are well documented for X = O,[8b,11] S[12] but less for X = CH$_2$.[13−15]

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* To whom correspondence should be addressed at Fachbereich Chemie der Universität Oldenburg, Carl-von-Ossietzky-Strasse 9-11, D-26111 Oldenburg, Germany.

(1) Reviews: (a) Beckhaus, R. *Angew. Chem.* **1997**, *109*, 694−722; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 686−713. (b) Beckhaus, R.; Oster, J.; Sang, J.; Strauss, I.; Wagner, M. *Synlett* **1997**, 241−249. (c) Beckhaus, R. *J. Chem. Soc., Dalton Trans.* **1997**, 1991−2001.

(2) Selected examples: (a) Beckhaus, R.; Flatau, S.; Troyanov, S. I.; Hofmann, P. *Chem. Ber.* **1992**, *125*, 291−299. (b) Beckhaus, R.; Strauss, I.; Wagner, T.; Kiprof, P. *Angew. Chem.* **1993**, *105*, 281−283; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 264−266. (c) Beckhaus, R. In *Organic Synthesis via Organometallics (OSM 4), Proceedings of the Fourth Symposium in Aachen, July 15 to 18, 1992*; Enders, D., Gais, H.-J., Keim, W., Eds.; Vieweg Verlag: Braunschweig, Germany, 1993; pp 131−149. (d) Beckhaus, R.; Zimmermann, C.; Wagner, T.; Herdtweck, E. *J. Organomet. Chem.* **1993**, *460*, 181−189. (e) Beckhaus, R.; Strauss, I.; Wagner, T. *J. Organomet. Chem.* **1994**, *464*, 155−161. (f) Beckhaus, R.; Oster, J.; Wagner, T. *Chem. Ber.* **1994**, *127*, 1003−1013. (g) Beckhaus, R.; Sang, J.; Oster, J.; Wagner, T. *J. Organomet. Chem.* **1994**, *484*, 179−190. (h) Beckhaus, R.; Strauss, I.; Wagner, T. *Angew. Chem.* **1995**, *107*, 738−740; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 688−690. (i) Beckhaus, R.; Oster, J. *Z. Anorg. Allg. Chem.* **1995**, *621*, 359−364. (j) Beckhaus, R.; Oster, J.; Loo, R. *J. Organomet. Chem.* **1995**, *501*, 321−326. (k) Beckhaus, R.; Sang, J.; Wagner, T.; Ganter, B. *Organometallics* **1996**, *15*, 1176−1187. (l) Beckhaus, R.; Oster, J.; Kempe, R.; Spannenberg, A. *Angew. Chem.* **1996**, *108*, 1636−1638; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1565−1567. (m) Beckhaus, R.; Sang, J.; Englert, U.; Böhme, U. *Organometallics* **1996**, *15*, 4731−4736.

(3) Luinstra, G. A.; Teuben, J. H. *Organometallics* **1992**, *11*, 1793−1801.

(4) (a) Janssen, M. D.; Herres, M.; Zsolnai, L.; Spek, A. L.; Grove, D. M.; Lang, H.; van Koten, G. *Inorg. Chem.* **1996**, *35*, 2476−2483. (b) Lang, H.; Weinmann, M. *Synlett* **1996**, 1−10. (c) Janssen, M. D.; Köhler, K.; Herres, M.; Dedieu, A.; Smeets, W. J. J.; Spek, A. L.; Grove, D. M.; Lang, H.; van Koten, G. *J. Am. Chem. Soc.* **1996**, *118*, 4817−4829.

(5) Beckhaus, R.; Oster, J.; Ganter, B.; Englert, U. *Organometallics* **1997**, *16*, 3902−3909.

(6) Ott, K. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 5922−5923.

(7) Werner, H. *Angew. Chem.* **1990**, *102*, 1109−1121; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1077−1089.

(8) (a) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*, 2nd ed.; Walter de Gruyter: Berlin, 1995. (b) Horwitz, C. P.; Shriver, D. F. *Adv. Organomet. Chem.* **1984**, *23*, 219−305.

(9) Broadhurst, P. V. *Polyhedron* **1985**, *4*, 1801−1846.

(10) (a) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197−257. (b) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59−128. (c) Werner, H.; Wolf, J.; Müller, G.; Krüger, C. *J. Organomet. Chem.* **1988**, *342*, 381−398.

(11) Cotton, F. A. *Prog. Inorg. Chem.* **1976**, *21*, 1−28.

(12) Doyle, R. A.; Daniels, L. M.; Angelici, R. J.; Stone, F. G. A. *J. Am. Chem. Soc.* **1989**, *111*, 4995−4997.

(13) (a) El Amouri, H.; Gruselle, M. *Chem. Rev.* **1996**, *96*, 1077−1103. (b) Kern, U.; Kreiter, C. G.; Müller-Becker, S.; Frank, W. *J. Organomet. Chem.* **1993**, *444*, C31−C33. (c) Akita, M.; Sugimoto, S.; Takabuchi, A.; Tanaka, M.; Moro-oka, Y. *Organometallics* **1993**, *12*, 2925−2932.

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Chart 1

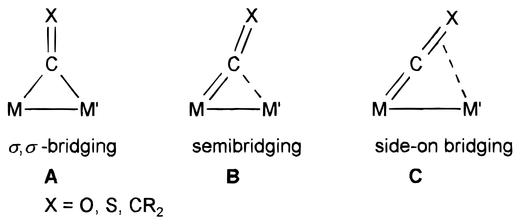


Table 1. Products from Reactions of 2 with 4

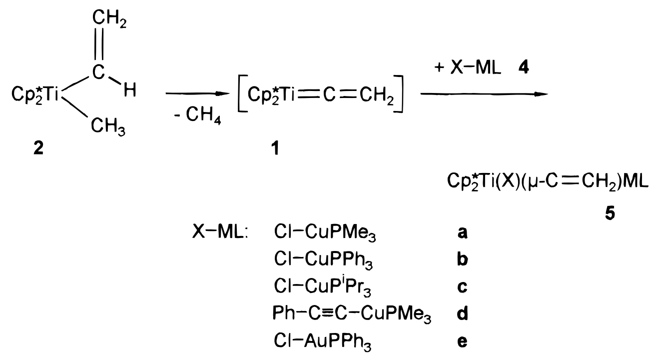
	X–M′–L			products			
	X	M′	L		yield (%)	color	mp (°C)
4a	Cl	Cu	PMe_3	**5a**	48	red	93–95 dec
4b	Cl	Cu	PPh_3	**5b**	36	red	137–140 dec
4c	Cl	Cu	$P(i\text{-}Pr)_3$	**5c**	46	red	145–147 dec
4d	PhCC	Cu	PMe_3	**5d**	40	yellow	180–182 dec
4e	Cl	Au	PPh_3	**5e**	38	red	109; 85 dec[a]

[a] Starting point of slow decomposition.

Moreover, complexes of the *semibridging* type **B,** usually characterized by an available filled orbital on M′ which donates into the acceptor orbitals of the bridging ligand, are known for CO[16] and CS complexes.[17] To our knowledge, a Mo–Ru complex is the only known example of a semibridging vinylidene.[14] Remarkably, only for complexes of type **C** ($X = CH_2$)[18] has an unusual vinylidene-acetylene rearrangement been observed.

Results

The vinylmethyltitanium derivative **2** reacts in THF with the tetrameric copper complexes **4a–d** or the gold complex **4e** (Ti:M = 1:1), within the temperature range 0–20 °C, to liberate methane, giving the binuclear complexes **5a–e** (Table 1).



The titanium–copper complexes **5a–d** can be isolated from benzene solutions as red or yellow crystals which are stable in air for a few minutes. The stability of the μ-vinylidene complexes **5** is influenced significantly by the phosphine ligand used. Exchange of PMe_3 in **5a** with PPh_3 or, especially, with $P(i\text{-}Pr)_3$ leads to an increase in the thermal stability in both solution and the solid state. A stabilization is also observed when the chloride is changed to a phenylacetylide group. Precipitation of metallic copper is observed for **5a** in solution at −23 °C, although **5b** is considerably more stable at this temperature, and **5c** and **5d** are stable at room temperature for several hours. The synthesis of a silver complex analogous to **5a** by reacting **2** with $[ClAgPMe_3]_4$[19] in THF at −50 °C led to a spontaneous precipitation of metallic silver.

The constitution of **5** can be deduced from spectroscopic data (Table 2). The $\mu\text{-}C{=}CH_2$ protons were detected in the ^1H NMR spectra as two separate signals, each split into a doublet of doublets by HH and PH couplings. The differences $\Delta = |\delta(H^1) - \delta(H^2)|$ for the protons of the *exo*-methylene group in **5a–d** were very small (0.52–0.16) compared to those in methylenemetallacyclobutane structures.[2f,h,j,m] In the ^{13}C NMR spectra, very low-field doublets at δ 329 (**5a–d**) and δ 300 ppm (**5e**) were found for the bridging carbon atom. The J_{PC} value in **5e** of 43.5 Hz is relatively large;[20] similar J_{PC} values were observed in *semi*bridged W(μ-CS)Au complexes.[17] ^{13}C NMR and IR data suggest that the coordination mode of the acetylide group ($X = PhC{\equiv}C{-}$) in **5d** is of the $\mu\text{-}\sigma,\eta^2$ type. A coupling to phosphorus is found for the β-carbon and the C_i atom of the phenyl group (3.7, 3.0 Hz), indicating that the acetylide is π-bonded to the copper and σ-bonded to the titanium center. The $\nu(C{\equiv}C)$ stretching vibration for **5d** at 1926 cm^{-1} is typical for μ-acetylide complexes.[21]

The values of the C=C stretching vibrations lie in the region observed for other μ-vinylidene complexes.[22] The only previously known Ti–Cu μ-vinylidene complex[4c,23] has a vibration at 1591 cm^{-1}.

MS data showed the expected molecular peaks for **5b** and **5d**. Notably, for **5e**, however, a titanium–gold fragment is observed as the basis peak at *m*/*z* 569, indicating a strong titanium–gold interaction, as is known to exist in homo- and heteronuclear gold complexes.[24]

Discussion

Titanium–late-transition-metal μ-vinylidene complexes have two limiting bonding modes, **A** and **C** (Chart 2). Structure **B** can be viewed as intermediate between the σ^2 (**A**) and the *side-on* bridging type (**C**).

Compared with side-on or semibridged vinylidenes,[10a] which should possess strong carbenic character similar

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(14) Boese, R.; Huffmann, M. A.; Vollhardt, K. P. C. *Angew. Chem.* **1991**, *103*, 1542–1543; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1463–1464.

(15) (a) Alonso, F. J. G.; Riera, V.; Ruiz, M. A.; Tiripicchio, A.; Camellini, M. T. *Organometallics* **1992**, *11*, 370–386. (b) Froom, S. F. T.; Green, M.; Mercer, R. J.; Nagle, K. R.; Orpen, A. G.; Rodrigues, R. A. *J. Chem. Soc., Dalton Trans.* **1991**, 3171–3183. (c) Doherty, N. M.; Elschenbroich, C.; Kneuper, H.-J.; Knox, S. A. R. *J. Chem. Soc., Chem. Commun.* **1985**, 170–171.

(16) (a) Crabtree, R. H.; Lavin, M. *Inorg. Chem.* **1986**, *25*, 805–812. (b) Winter, M. J. *Adv. Organomet. Chem.* **1989**, *29*, 101–162.

(17) Kim, H. P.; Kim, S.; Jacobson, R. A.; Angelici, R. J. *J. Am. Chem. Soc.* **1986**, *108*, 5154–5158.

(18) Ti/M′ derivatives:[2f] Mo–Mo;[15b] Mercer, R. J.; Green, M.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1986**, 567–569.

(19) Schmidbaur, H.; Adlkofer, J.; Schwirten, K. *Chem. Ber.* **1972**, *105*, 3382–3388.

(20) Mann, B. E. *Adv. Organomet. Chem.* **1974**, *12*, 135–213.

(21) (a) Lang, H.; Herres, M.; Zsolnai, L.; Imhof, W. *J. Organomet. Chem.* **1991**, *409*, C7–C11. (b) Lang, H.; Blau, S.; Pritzkow, H.; Zsolnai, L. *Organometallics* **1995**, *14*, 1850–1854. (c) Janssen, M. D.; Herres, M.; Zsolnai, L.; Grove, D. M.; Spek, A. L.; Lang, H.; van Koten, G. *Organometallics* **1995**, *14*, 1098–1100.

(22) $\nu(C{=}C)$ (cm^{-1}) of $M(\mu\text{-}\sigma^2\text{-}C{=}CR_2)M'$ complexes: Rh–Rh, 1575;[22a] Mn–Mn, 1542;[22b] Mn–Re, 1552.[22c] (a) Esteruelas, M. A.; Lahoz, F. J.; Onate, E.; Oro, L. A.; Rodriguez, L. *Organometallics* **1993**, *12*, 4219–4222. (b) Folting, K.; Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1979**, *18*, 3483–3486. (c) Kolobova, N. E.; Antonova, A. B.; Khitrova, O. M. *J. Organomet. Chem.* **1978**, *146*, C17–C18.

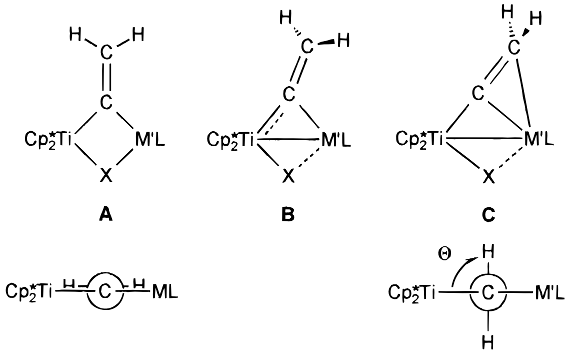
(23) Janssen, M. D.; Smeets, W. J. J.; Spek, A. L.; Grove, D. M.; Lang, H.; van Koten, G. *J. Organomet. Chem.* **1995**, *505*, 123–126.

(24) Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1996**, 561–566.

Table 2. Selected NMR Data for the μ-Vinylidene Complexes 5

		^{13}C NMR (ppm)		^{1}H NMR ([ppm)			
	IR (cm^{-1}) ν(C═C)	μ-**C**(═CH$_2$)	μ-(═**C**H$_2$)	$^{2}J_{HH}$ (Hz)	J_{PH} (Hz)	Ti−μ-C(═CH_2)−M	
5a	1540 w	330.1	114.5	9.4	5.2	6.16	5.70
5b	1547 m	328.7	116.4	9.3	5.9	6.16	5.72
5c	1548 m	329.8	115.7	9.1	4.9	6.31	5.79
5d	1548 m	329.2	113.9	8.6	2.9	6.16	6.00
5e	1544 m	300.5	118.5			6.71	5.62

Chart 2



to terminal vinylidenes, μ-σ^2-C═CR$_2$ groups are generally characterized by a high-field shift of the α-carbon atom in the ^{13}C NMR spectrum. ^{13}C NMR data of the terminal titanium−vinylidene complex **1** are not available, but analogous titanium−alkylidene and −allenylidene complexes show values in the range δ 265−313 for the carbene C atom.[1a,25] Remarkably, in comparable carbyne semibridged tungsten−gold complexes, the chemical shifts for the μ-C resonances are similar to those found in mononuclear precursor molecules.[26]

In addition, structures **A** and **C** can be distinguished by the value of the twist angle Θ (Chart 2). Due to the small value of Θ for **A,** which is generally ≤10°,[22b,27] the protons of the μ-σ^2-C═CH$_2$ group should be inequivalent. On the other hand, for the side-on-bonded structure **C** chemically equivalent protons are expected, for the twist angle Θ ≈ 90°.

The observed chemical shifts for complexes **5a**−**e** (δ 300−330) do not agree with a μ-σ^2-bonding mode. Moreover, the small Δ values (|δ(H^1) − δ(H^2)|; Table 2) for these complexes indicate only a small twist around the C═C bond, so that **5a**−**e** are best described as the semibridging type **B**. A comparable effect was found for the vinylidene-bridged Ru−Mo complexes undergoing a ligand-dependent transformation between a side-on coordination mode and a semibridged structure (|ΔΘ| = 90 °).[14]

Suitable crystals of **5e** for an X-ray diffraction study were obtained from benzene, as an adduct containing two solvent molecules per asymmetric unit. A PLATON plot[28] of **5e** is shown in Figure 1, and relevant bond lengths and angles are given in Table 3. The molecular packing is shown in Figure 2.

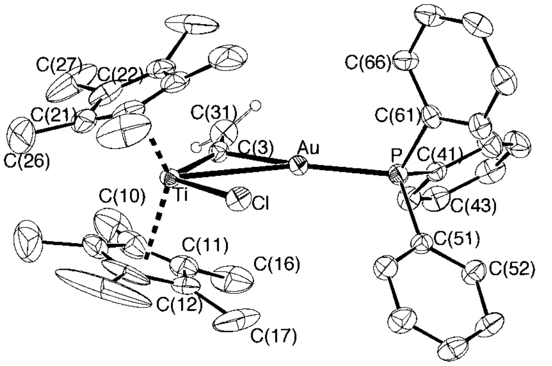


Figure 1. Platon[28] plot of the molecular structure of complex **5e** with thermal ellipsoids at the 30% probability level.

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

Ti−C3	2.023(5)	Au−P	2.280(1)
Ti−Au	2.9547(8)	Au···Cl	2.938(5)
Ti−Cl	2.499(1)	Ti−[Cp]	2.133
C3−C31	1.324(7)	Ti−[Cp][a]	2.139
C3−Au	2.075(5)		
C3−Ti−Au	44.6(1)	Ti−Au−P	156.64(4)
C3−Ti−Cl	109.0(1)	P−Au−C3	159.7(1)
Ti−C3−Au	92.3(2)	Ti−Au−C3	43.2(1)
Ti−C3−C31	152.0(5)		

[a] Ti−[Cp] is the perpendicular line from the best plane through the cyclopentadienyl ring directed toward the titanium center.

The structural analysis established the expected μ-vinylidene structure with trigonal-planar coordination at the gold atom. The titanium, the gold, and the C3 atom are part of an acute triangle, characterized by the right angle Ti−C3−Au (92.3°) and two nearly 45° angles (Au−Ti−C3, 44.6(1)°; Ti−Au−C3, 43.2(1)°). The chloride is not bonded to the gold atom (the Au−Cl distance is in a nonbonding range (2.938(5) Å)).[29] The Ti−Cl distance in **5e** is longer than expected for terminal titanium halides.[30] A similar elongation of the Ti−Cl bond was observed in titanocene complexes with additional donating ligands.[31] For complex **5e** this elongation is caused by the Ti−Au interaction.

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(25) (a) Binger, P.; Müller, P.; Benn, R.; Mynott, R. *Angew. Chem.* **1989**, *101*, 647−648; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 610−611. (b) van Doorn, J. A.; van der Heijden, H.; Orpen, A. G. *Organometallics* **1994**, *13*, 4271−4277. (c) van der Heijden, H.; Hessen, B. *J. Chem. Soc., Chem. Commun.* **1995**, 145−146. (d) Binger, P.; Müller, P.; Wenz, R.; Mynott, R. *Angew. Chem.* **1990**, *102*, 1070−1071; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1037−1038.

(26) Green, M.; Howard, J. A. K.; James, A. P.; Nunn, C. M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1987**, 61−72.

(27) Kolobova, N. E.; Ivanov, L. L.; Zhvanko, O. S.; Aleksandrov, G. G.; Struchkov, Y. T. *J. Organomet. Chem.* **1982**, *228*, 265−272.

(28) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.

(29) Characteristic Au−Cl bonds (Å): R$_3$PSAu−Cl, 2.2707(8); R$_3$PAu−Cl, 2.2879(10);[29a] (Me$_2$N)$_3$PAu−Cl, 2.289(4);[29b] Me$_3$PAu−Cl, 2.310;[29c] Et$_3$PAu−Cl. 2.305(8).[29d] (a) Schneider, W.; Bauer, A.; Schier, A.; Schmidbaur, H. *Chem. Ber.* **1997**, *130*, 1423−1426. (b) Bauer, A.; Mitzel, N. W.; Schier, A.; Rankin, D. W. H.; Schmidbaur, H. *Chem. Ber.* **1997**, *130*, 323−328. (c) Angermaier, K.; Zeller, E.; Schmidbaur, H. *J. Organomet. Chem.* **1994**, *472*, 371−376. (d) Tiekink, E. R. T. *Acta Crystallogr.* **1989**, *C45*, 1233−1234.

(30) Terminal Ti−Cl bonds (Å): (C$_5$Me$_4$H)$_2$TiCl, 2.317;[30a] Cp*$_2$TiCl, 2.363;[30b] Cp*$_2$TiCl$_2$, 2.352(1), 2.346(1).[30c] (a) Troyanov, S. I.; Rybakov, V. B.; Thewalt, U.; Varga, V.; Mach, K. *J. Organomet. Chem.* **1993**, *447*, 221−225. (b) Pattiasina, J. W.; Heeres, H. J.; Van Bolhuis, F.; Meetsma, A.; Teuben, J. H.; Spek, A. L. *Organometallics* **1987**, *6*, 1004−1010. (c) McKenzie, T. C.; Sanner, R. D.; Bercaw, J. E. *J. Organomet. Chem.* **1975**, *102*, 457−466.

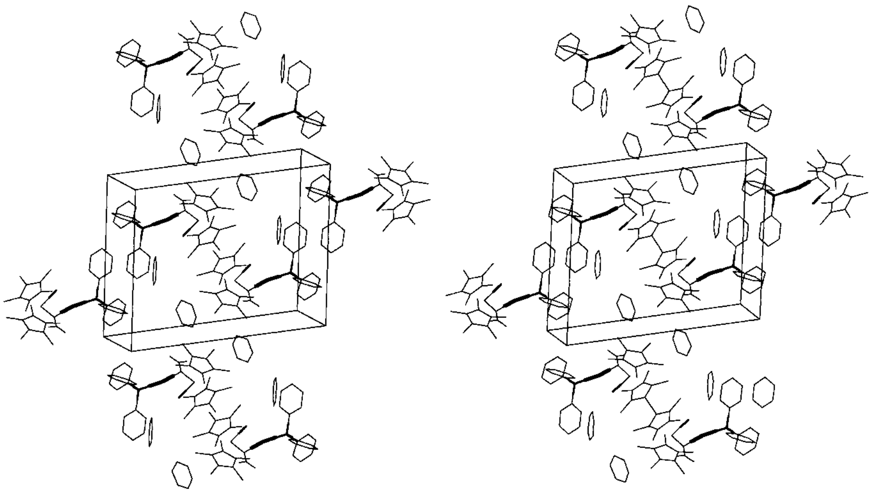

Figure 2. SCHAKAL drawing[41] of the molecular packing of **5e**·$2C_6H_6$.

The Au−P distance of 2.280(1) Å is similar to those observed in other gold phosphine complexes.[32] The NMR measurements suggested that the Ti−C bond in **5** exhibits a considerable double-bond character. The short Ti−C3 bond of 2.023(5) Å and the large Ti−C3−C31 angle of 152.0(5)° confirmed this hypothesis. This is the shortest bond length of all the hitherto known subsequent products of **1**.[33] The Ti−C bond length falls in the range established for complexes with Ti−C double-bond character.[34]

Many heterometallic complexes containing Au−M bonds have been reported.[35,36] Complexes with a Ti−Au interaction are rare. The first examples were prepared from low-valent carbonyls[37] or chelating titanocene acetylides.[38] The Ti−Au distance of 2.9547(8) Å in **5e** is in a range typical for a bonding interaction. In the $[(OC)_6Ti{-}AuPEt_3]$ anion, a short value of 2.719(1) Å was found for the Ti−Au distance.[37] Longer titanium−gold distances (2.975(1)−3.007(2) Å) were observed for Ti−Au tweezer complexes obtained from $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2]$ and gold(I) derivatives.[38] Due to the Ti−Au interaction in **5e**, the titanium atom is formally five-coordinate, and as a consequence the C3−Ti−Cl angle is enlarged to 109(1)° compared with those of titanacycles[1a] or even acyclic Cp_2TiX_2 derivatives.[39] In the five-coordinate titanocene complexes $Cp_2Ti(\eta^2\text{-}XY)Z$, comparable X−Ti−Z angles were found: e.g., $Cp_2Ti(\eta^2\text{-}C(O)CH_3)Cl$ (112.2(3)°),[31] $Cp_2Ti(\eta^2\text{-}C(O)CH_3)GePh_3$ (109.0(4)°),[40a] and $Cp_2Ti(\eta^2\text{-}CH_2OCH_3)Cl$ (116.0(1)°).[40b] As a result of the coordination of the gold atom to both the titanium and C3 atoms, the Ti−Au−P as well as the C3−Au−P angles are nonlinear (156.64(4), 159.7(1)°).

The solid-state structure of **5e**·2 C_6H_6 is typical of a van der Waals crystal: the closest intermolecular contacts between neighboring complex molecules occur along the *c* direction involving C18···C18 distances of 3.30(2) Å between the Cp* rings. Short contacts (C55···C55 = 3.64(1)) are found between phenyl groups of the Ph_3P ligands—both close to crystallographic inversion centers. The benzene molecules fill the voids between the complex molecules, forming channels along direction *a*. Under vacuum, the complex loses solvent and the crystals are gradually destroyed.

Considering the results of both the NMR studies and the X-ray analysis of **5e**, the best structure of **5a**−**e** is the semibridging structure **B** (Scheme 2). This structure type is probably preferred for the following reasons. (1) In **B** especially the vinylidene ligand is able to realize strong π-acceptor properties.[2a] (2) Low-valent titanium complexes exhibit stronger back-donation to π-acceptor ligands compared to Au(I) or Cu(I) complexes.[42] (3) The metal-centered LUMO of the titanaallene fragment is strongly oriented in the direction of the open coordination side,[2a] leading to a Ti−M bond.

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[31] Ti−Cl bonds in titanocene complexes with donating ligands (Å): $Cp(C_5Me_4CH_2CH_2NMe_2)TiCl$, 2.4610(7);[5] $Cp_2Ti(\eta^2\text{-}C(O)CH_3)Cl$, 2.494(6). Fachinetti, G.; Floriani, C.; Stoeckli-Evans, H. *J. Chem. Soc., Dalton Trans.* **1977**, 2297−2302.

[32] Au−P (Å): $PhAu{-}PPh_3$, 2.296(2),[32a] 2.284(1);[32b] $PhCCAu{-}PPh_3$, 2.276(5), 2.282(4);[32c] $(OC)_6VAu{-}PPh_3$, 2.260(3).[32d] (a) Hong, X.; Cheung, K.-K.; Guo, C.-X.; Che, C.-M. *J. Chem. Soc., Dalton Trans.* **1994**, 1867−1871. (b) Riley, P. E.; Davis, R. E. *J. Organomet. Chem.* **1980**, *192*, 283−291. (c) Bruce, M. I.; Duffy, D. N. *Aust. J. Chem.* **1986**, *39*, 1697−1701. (d) Drew, M. G. B. *Acta Crystallogr.* **1982**, *B38*, 254−255.

[33] In metallacycles derived from the $Cp^*_2Ti{=}C{=}CH_2$ intermediate Ti−C distances of 2.068(6)−2.161(5) Å are found (see Table 4 in ref 1a).

[34] Known Ti−C double-bond lengths are 1.757(7)−2.051(2) Å. For a review, ref 1a. (a) Krüger, C.; Mynott, R.; Siedenbiedel, C.; Stehling, L.; Wilke, G. *Angew. Chem.* **1991**, *103*, 1714−1715; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1668−1669. (b) De Angelis, S.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Angew. Chem.* **1995**, *107*, 1200−1202; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1092−1094. (c) van Doorn, J. A.; van der Heijden, H.; Orpen, A. G. *Organometallics* **1995**, *14*, 1278−1283. (d) Binger, P.; Müller, P.; Phillipps, P.; Gabor, B.; Mynott, R.; Herrmann, A. T.; Langhauser, F.; Krüger, C. *Chem. Ber.* **1992**, *125*, 2209−2212.

[35] Mingos, D. M. P.; Watson, M. J. *Adv. Inorg. Chem.* **1992**, *39*, 327−399.

[36] M: V,[32d] Mo,[36a] W,[36a] Mn,[36b] Re and Co,[36c] Ir and mixed clusters:[36d] (a) Haines, R. J.; Nyholm, R. S.; Stiddard, M. H. B. *J. Chem. Soc. A* **1968**, 46−47. (b) Coffey, C. E.; Lewis, J.; Nyholm, R. S. *J. Chem. Soc.* **1964**, 1741−1749. (c) Blundell, T. L.; Powell, H. M. *J. Chem. Soc. A* **1971**, 1685−1690. (d) Ellis, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 6106−6110.

[37] Fischer, P. J.; Young, V. G., Jr.; Ellis, J. E. *Chem. Commun.* **1997**, 1249−1250.

[38] (a) Lang, H.; Köhler, K.; Zsolnai, L. *Chem. Commun.* **1996**, 2043−2044. (b) Köhler, K.; Silverio, S. J.; Hyla-Kryspin, I.; Gleiter, R.; Zsolnai, L.; Driess, A.; Huttner, G.; Lang, H. *Organometallics* **1997**, *16*, 4970−4979.

[39] Characteristic values for C−Ti-X (deg): $Cp_2^*Ti(CH{=}CH_2)F$, 93.5(8);[2g] $Cp^*_2Ti(CH{=}CH_2)OR$, 96.36(9);[2e] $Cp^*_2TiCl_2$, 92.94(4).[30c] Review: Cozak, D.; Melnik, M. *Coord. Chem. Rev.* **1986**, *14*, 53−99.

[40] (a) Harrod, J. F.; Malek, A.; Rochon, F. D.; Melanson, R. *Organometallics* **1987**, *6*, 2117−2120. (b) Erker, G.; Schlund, R.; Krüger, C. *J. Organomet. Chem.* **1988**, *338*, C4−C6.

[41] Keller, E. SCHAKAL 88, Program for the Graphical Representation of Crystallographie and Molecular Models; University of Freiburg, Freiburg, Germany, 1988.

[42] Aubke, F.; Wang, C. *Coord. Chem. Rev.* **1994**, *137*, 483−524.

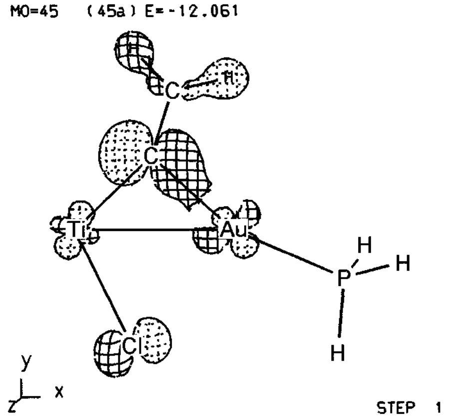

Figure 3. HOMO of the model complex $Cp_2Ti(Cl)(\mu\text{-}C{=}CH_2)AuPH_3$.

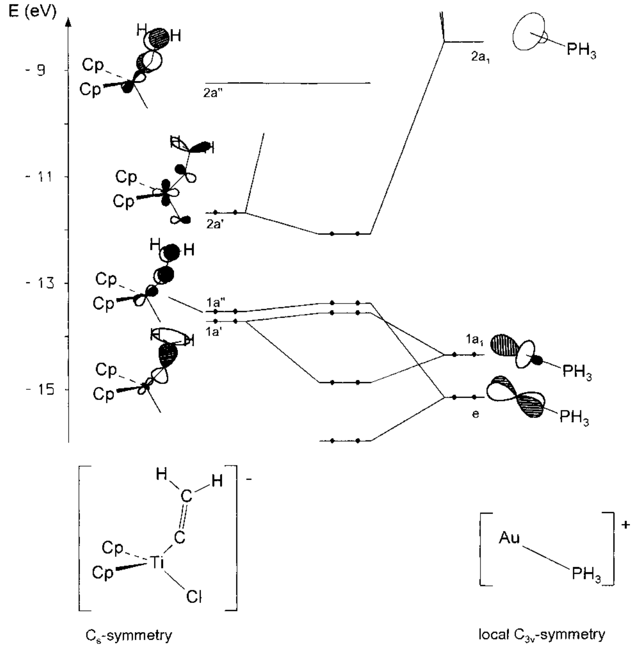

Figure 4. EH interaction diagram between the valence MO's of $[Cp_2TiCl(C{=}CH_2)]^-$ and $AuPH_3^+$.

The semibridging description was also supported by extended Hückel calculations on $Cp_2Ti(Cl)(\mu\text{-}CCH_2)$-$AuPH_3$. The HOMO is formed by the interaction of the LUMO ($2a_1$) of $AuPH_3^+$ with the occupied 2a′ orbital from the $Cp_2Ti(Cl)(C{=}CH_2)$ anion (Figure 3). The HOMO in Figure 3 shows bonding interactions between Ti−C, Au−C, and Ti−Au. Further interaction of a π-type is observed between a d-orbital on gold (e) and the 1a″ orbital. The latter represents bonding orbital coefficients for the carbon−carbon double bond plus the d orbital on titanium (Figure 4). Full details, including ab initio and DFT calculations, will be the subject of a forthcoming paper.[43]

Finally, it is noted that the vinylidene-bond chemistry discussed above could not be realized in the reaction of **2** with Me_2AlCl. Thus, **2** was found to react with Me_2AlCl to afford $Cp^*{}_2TiCl$ as the only titanium-containing product. In contrast to the reaction of Me_2AlCl with titanocene methyl complexes,[44] the formation of a vinylidene species analogous to the Tebbe reagent[45] was not observed.

Conclusions

The present study reveals several interesting bonding features of titanium−copper and −gold μ-vinylidene complexes derived from the reaction of the titanocene−vinylidene intermediate $[Cp^*{}_2Ti{=}C{=}CH_2]$ (**1**) and late-transition-metal complexes. Complexes **5a**−**e** are the first examples of a vinylidene complex stabilized by a M−Ti bond. In **5e** a relatively short μ-C−Ti separation is accompanied by a relatively long μ-C−Au distance, so that the μ-$C{=}CH_2$ ligand is unsymmetrically bridging the Ti−Au bond.

Experimental Section

General Considerations. The preparation and handling of the described compounds was performed with rigorous exclusion of air and moisture under a nitrogen atmosphere using standard vacuum line and Schlenk techniques. All solvents were dried and distilled under a nitrogen atmosphere. ^1H and ^{13}C NMR spectra were recorded on a Varian Unity 500 or Varian VXR-300 spectrometer. Chemical shifts are reported in ppm and referenced to residual protons in deuterated solvents. Mass spectroscopic analyses were performed on a Finnigan MAT 95 mass spectrometer. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer 1720 X FT-IR spectrometer. Elemental analyses were carried out at the Analytische Laboratorien in Lindlar, Germany. The metal complexes **2**[2i] and **4b**[46] were prepared by literature procedures or purchased from Aldrich.

Bis(η^5-pentamethylcyclopentadienyl)chloro(μ-vinylidene)(trimethylphosphane-κ*P*)coppertitanium (5a). To a suspension of 75 mg of CuCl (0.758 mmol) in 20 mL of THF was added 80 μL of PMe_3 (0.788 mmol) at room temperature. The resulting solution was cooled to −40 °C, and 290 mg of $Cp_2^*Ti(CH{=}CH_2)Me$ (**2**; 0.806 mmol), dissolved in 20 mL of THF, was added. During warming to room temperature the solution became red at 0 °C, and traces of metallic copper precipitated. After the mixture was stirred for 1 h at room temperature, the solvent was removed under reduced pressure. The residue was extracted with 20 mL of *n*-hexane and filtered. The red filtrate was evaporated to 5 mL, and at −23 °C red crystals of **5a** were obtained (190 mg, 48%; mp 93−95 °C dec). ^1H NMR ($C_6D_5CD_3$, 500 MHz, −20 °C): δ 0.69 (dd, 9H, $^2J_{PH}$ = 6.7 Hz, $P(CH_3)_3$), 1.88 (s, 30 H, $C_5(CH_3)_5$), 5.70 (dd, $^2J_{HH}$ = 9.4 Hz, $^4J_{PH}$ = 5.4 Hz, 1H, $=CH_2$), 6.16 (dd, $^2J_{HH}$ = 9.4 Hz, $^4J_{PH}$ = 5.4 Hz, 1H, $=CH_2$). $^{13}C\{^1H\}$ NMR ($C_6D_5CD_3$, 125 MHz, −40 °C): δ 13.1 (s, $C_5(CH_3)_5$), 14.6 (d, $^1J_{CP}$ = 21.3 Hz, $P(CH_3)_3$), 113.5 (s, $C_5(CH_3)_5$), 114.1 (d, $^3J_{CP}$ = 4.3 Hz, $=CH_2$), 329.4 (d, $^2J_{CP}$ = 12.8 Hz, $C{=}CH_2$). EI-MS (70 eV): *m*/*e* (I_{rel}) 353 (100) ($(C_5(CH_3)_5)_2TiCl^+$), 317 (45) ($(C_5(CH_3)_5)(C_5(CH_3)_4CH_2)Ti^+$), 218 (42) ($(C_5(CH_3)_5)TiCl^+$). IR (KBr): 1540 w (ν(C=C)), 1428 s (δ(CH_3), $P(CH_3)_3$), 1373 s (δ(CH_3), $P(CH_3)_3$), 1018 m ($\delta(CH_2)_{oop}$), 951 s (δ(CH_3), $P(CH_3)_3$), 799 s cm^{-1} (ν(P−C)). Anal. Calcd for $C_{25}H_{41}ClPCuTi$ (519.10): C, 57.84; H, 7.90. Found: C, 57.85; H, 7.98.

Bis(η^5-pentamethylcyclopentadienyl)chloro(μ-vinylidene)(triphenylphosphane-κ*P*)coppertitanium (5b). To a solution of 360 mg of $Cp_2^*Ti(CH{=}CH_2)Me$ (**2**; 1.00 mmol) in 40 mL of THF was added 330 mg of $[Ph_3PCuCl]_4$ (**4b**; 0.228 mmol) at −40 °C. During slow warming to room temperature,

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[43] Beckhaus, R.; Böhme, U. Unpublished results.

[44] Finch, W. C.; Anslyn, E. V.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 2406−2413.

[45] (a) Yoshida, T.; Negishi, E. *J. Am. Chem. Soc.* **1981**, *103*, 1276−1277. (b) Dennehy, R. D.; Whitby, R. J. *J. Chem. Soc., Chem. Commun.* **1992**, 35−36.

[46] Reichle, W. T. *Inorg. Chim. Acta* **1971**, *5*, 325−332.

the solution became red and traces of metallic copper precipitated at + 10 °C. After the mixture was stirred for 3 h at room temperature, the solvent was removed under reduced pressure, leaving a waxy solid, which was extracted with 20 mL of toluene and filtered. The resulting red solution was reduced in volume to 5 mL and stored at −23 °C. The product was obtained as a red, microcrystalline solid (230 mg, 36%; mp 137−140 °C dec). ^{1}H NMR ($C_6D_5CD_3$, 500 MHz, −20 °C): δ 1.85 (s, 30 H, $C_5(CH_3)_5$), 5.72 (dd, $^2J_{HH} = 9.3$ Hz, $^4J_{PH} = 5.1$ Hz, 1H, $=CH_2$), 6.16 (dd, $^2J_{HH} = 9.3$ Hz, $^4J_{PH} = 5.1$ Hz, 1H, $=CH_2$), 6.99 (m, 9H, *m*- + *p*-C_6H_5), 7.63 (m, 6H, *o*-C_6H_5). $^{13}C\{^1H\}$ NMR ($C_6D_5CD_3$, 125 MHz, −20 °C): δ 13.0 (s, $C_5(CH_3)_5$), 114.1 (s, $C_5(CH_3)_5$), 116.4 (d, $^3J_{CP} = 2.9$ Hz, $=CH_2$), 128.9 (d, $^3J_{CP} = 2.9$ Hz, *m*-C), 130.4 (s, *p*-C), 132.7 (d, $^1J_{CP} = 34.0$ Hz, *ipso*-C), 134.3 (d, $^1J_{CP} = 14.9$ Hz, *o*-C), 328.7 (d, $^2J_{CP} = 11.1$ Hz, $C=CH_2$). EI-MS (70 eV): *m/e* (I_{rel}) 704 (<1) (M^+), 353 (68) ($(C_5(CH_3)_5)_2TiCl^+$), 317 (30) ($(C_5(CH_3)_5)(C_5(CH_3)_4CH_2)$-$Ti^+$), 262 (100) ($PPh_3^+$), 218 (40) ($(C_5(CH_3)_5)TiCl^+$). IR (KBr): 3053 w ($\nu$(CH), Ph), 1547 m ($\nu$(C=C)), 1431 s ($\delta(Ph)_{ip}$), 1092 s ($\delta$(P−Ph)), 1017 m ($\delta(CH_2)_{oop}$), 693 s ($\nu$(P−C)), 522 s cm^{-1} ($\delta$(P−Ph)). Anal. Calcd for $C_{40}H_{47}ClCuPTi$: C, 68.08; H, 6.71. Found: C, 67.43; H: 6.89.

Bis(η^5-pentamethylcyclopentadienyl)chloro(μ-vinylidene)(triisopropylphosphane-κP)coppertitanium (5c). To a suspension of 85 mg of CuCl (0.859 mmol) in 10 mL of THF was added 168 mL of P(*i*-Pr)$_3$ (0.859 mmol) at room temperature. The resulting solution was cooled to −50 °C, and 350 mg of $Cp^*{}_2Ti(CH=CH_2)Me$ (**2**) (0.972 mmol) in 20 mL of THF was added. During slow warming, the solution became red at 0 °C. After the mixture was stirred for 1 h at room temperature, the solvent was removed under reduced pressure. The residue was extracted with 20 mL of toluene and filtered. The red filtrate was evaporated to 5 mL. At −23 °C red crystals of **5c** were obtained (240 mg, 46%; mp 145−147 °C dec). ^{1}H NMR (C_6D_6, 500 MHz, 25 °C): δ 1.04 (dd, 18H, $^3J_{PH} = 13.9$ Hz, $^2J_{HH} = 7.1$ Hz, CHC*H*$_3$), 1.72 (m, 3H, P−CH), 1.90 (s, 30 H, $C_5(CH_3)_5$), 5.79 (dd, $^2J_{HH} = 9.1$ Hz, $^4J_{PH} = 4.9$ Hz, 1H, $=CH_2$), 6.31 (dd, $^2J_{HH} = 9.1$ Hz, $^4J_{PH} = 4.9$ Hz, 1H, $=CH_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 63 MHz, 25 °C): δ 13.0 (s $C_5(CH_3)_5$), 20.0 (d, $^2J_{CP} = 4.7$ Hz, CH*C*H$_3$), 22.5 (d, $^1J_{CP} = 16.1$ Hz, P−CH), 113.5 (s, $C_5(CH_3)_5$), 114.1 (d, $^3J_{CP} = 4.3$ Hz, $=CH_2$), 329.4 (d, $^2J_{CP} = 12.8$ Hz, $C=CH_2$). IR (KBr): 1548 m cm^{-1} (ν(C=C)). Anal. Calcd for $C_{31}H_{53}ClPCuTi$ (603.16): C, 61.73; H, 8.79. Found: C, 62.12; H, 9.25.

Bis(η^5-pentamethylcyclopentadienyl)(μ-η^1:η^2-phenylethynyl)(μ-vinylidene)(trimethylphosphane-κP)coppertitanium (5d). To a solution of 120 mg of $[Cu-C\equiv C-Ph]_x$ (0.729 mmol) in 40 mL of THF was added a solution of 280 mg of $Cp_2{}^*Ti(CH=CH_2)Me$ (**2**; 0.778 mmol) and 74 μL (0.729 mmol) of PMe_3 in 20 mL of THF, at −30 °C. After the reaction mixture was warmed and stirred for 4 h at room temperature, a yellow suspension was formed. The solvent was removed under reduced pressure and the residue extracted with 15 mL of benzene. After filtration, the yellow solution was reduced in volume to 3 mL and stored at 7 °C. The product was obtained as yellow crystals (170 mg, 40%; 180−182 °C dec). ^{1}H NMR ($C_6D_5CD_3$, 500 MHz, −10 °C): δ 0.65 (dd, 9H, $^2J_{PH} = 6.7$ Hz, $P(CH_3)_3$), 1.88 (s, 30 H, $C_5(CH_3)_5$), 6.00 (dd, $^2J_{HH} = 8.6$ Hz, $^4J_{PH} = 2.9$ Hz, 1H, $=CH_2$), 6.16 (dd, $^2J_{HH} = 8.6$ Hz, $^4J_{PH} = 2.9$ Hz, 1H, $=CH_2$), 6.95 (t, $^3J_{HH} = 7.5$ Hz, 1H, *p*-H), 7.05 (t, $^3J_{HH} = 7.5$ Hz, 1H, *m*-H), 7.41 (t, $^3J_{HH} = 7.5$ Hz, 1H, *o*-H). $^{13}C\{^1H\}$ NMR ($C_6D_5CD_3$, 125 MHz, −10 °C): δ 13.0 (s, $C_5(CH_3)_5$), 14.0 (d, $^1J_{CP} = 21.3$ Hz, $P(CH_3)_3$), 110.2 (s, $C_5(CH_3)_5$), 113.9 (d, $^3J_{CP} = 7.5$ Hz, $=CH_2$), 125.2 (s, *p*-C), 128.4 (s, *m*-C), 129.7 (s, *o*-C), 131.5 (d, $^3J_{CP} = 3.0$ Hz, *ipso*-C), 131.7 (d, $^2J_{CP} = 3.7$ Hz, C−Ph), 160.6 (s, $C\equiv CPh$), 329.2 (d, $^2J_{CP} = 5.2$ Hz, $C=CH_2$). EI-MS (70 eV): *m/z* (I_{rel}) 584 (<1) (M^+), 446 (37) ($M^+ - CuPMe_3$), 420 (8) ($(C_5(CH_3)_5)_2TiC_2HPh^+$), 344 (15) ($(C_5(CH_3)_5)_2$-$TiC_2H_2^+$), 317 (100) ($(C_5(CH_3)_5)(C_5(CH_3)_4CH_2)Ti^+$). IR (KBr): 3047 w ($\nu$(CH), Ph), 1926 s ($\nu$(C≡C)), 1587 s ($\nu$(C−C), C_2Ph), 1548 m (ν(C=C)), 1427 m ($\delta(CH_3)$, $P(CH_3)_3$), 1370 m ($\delta(CH_3)$, $P(CH_3)_3$), 1019 m ($\delta(CH_2)_{oop}$), 951 s ($\delta(CH_3)$, $P(CH_3)_3$), 756 s cm^{-1} (ν(P−C)). Anal. Calcd for $C_{33}H_{46}PCuTi$: C, 67.78; H, 7.87. Found: C, 67.51; H, 7.94.

Table 4. Crystal Data, Data Collection Parameters and Convergence Results for 5e·2C_6H_6

formula	$C_{52}H_{59}AuClPTi$
fw	995.34
cryst syst	triclinic
space group (No.)	$P\bar{1}$ (2)
a, Å	9.711(2)
b, Å	14.947(3)
c, Å	17.746(2)
α, deg	98.67(2)
β, deg	104.59(2)
γ, deg	108.52(3)
U, Å^3	2288(2)
Z	2
d_{calc}, g cm^{-3}	1.44
μ, cm^{-1}	3.495
θ_{max}, deg	27
min transmissn	0.759
max transmissn	1.000
cryst dimens, mm^3	0.44 × 0.28 × 0.20
no. of rflns	10 525
no. of indep obs rflns, $I > \sigma(I)$	8788
no. of params refined	505
R^a	0.048
$R_w{}^b$	0.052
GOF^c	1.436
res el density, e Å^{-3}	1.78 (close to Au)

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w^{-1} = \sigma^2(F_o)$. ^{c} GOF $= [\sum w(|F_o| - |F_c|)^2/n_{obs} - n_{var}]^{1/2}$; n_{obs} = no. of observations, n_{var} = no. of variables refined.

Bis(η^5-pentamethylcyclopentadienyl)chloro(μ-vinylidene)(triphenylphosphane-κP)goldtitanium (5e). To 330 mg of $Cp_2{}^*Ti(CH=CH_2)Me$ (**2**; 0.917 mmol) was added a solution of 430 mg of $[Ph_3PAuCl]$ (0.869 mmol) in 20 mL of THF at −35 °C. During slow heating to room temperature, the solution turned red and formation of a gold mirror occurred. After the mixture was stirred for 1 h at room temperature, the solution was evaporated to dryness and the residue extracted with 20 mL of benzene. After the resulting red solution was reduced to 5 mL and cooled to 7 °C, the product was obtained as red crystals (280 mg, 38%; mp 109 °C, dec 85 °C). ^{1}H NMR ($C_6D_5CD_3$, 500 MHz, −20 °C): δ 1.90 (s, 30 H, $C_5(CH_3)_5$), 5.62 (m, 1H, $=CH_2$), 6.71 (m, 1H, $=CH_2$), 6.96 (m, 9H, *m*- + *p*-C_6H_5), 7.65 (m, 6H, *o*-C_6H_5). $^{13}C\{^1H\}$ NMR ($C_6D_5CD_3$, 125 MHz, −20 °C): δ 13.5 (s, $C_5(CH_3)_5$), 117.4 (s, $C_5(CH_3)_5$), 118.5 (d, $^3J_{CP} = 3.6$ Hz, $=CH_2$), 128.8 (d, $^3J_{CP} \approx 10$ Hz (hidden under solvent), *m*-C), 130.9 (d, $^4J_{CP} = 2.0$ Hz, *p*-C), 132.3 (d, $^1J_{CP} = 48.3$ Hz, *ipso*-C), 134.8 (d, $^2J_{CP} = 14.5$ Hz, *o*-C), 300.5 (d, $^2J_{CP} = 43.5$ Hz, $C=CH_2$). EI-MS (70 eV): *m/z*(I_{rel}) 569 (100) ($M^+ - (C_5(CH_3)_5) - Cl$), 353 (38) ($(C_5(CH_3)_5)_2$-$TiCl^+$), 317 (20) ($(C_5(CH_3)_5)(C_5(CH_3)_4CH_2)Ti^+$), 262 (76) ($PPh_3^+$), 135 (81) ($(C_5(CH_3)_5)^+$). IR (KBr): 3053 m ($\nu$(CH), Ph), 1544 m ($\nu$(C=C)), 1435 s ($\delta(Ph)_{ip}$), 1099 s ($\delta$(P−Ph)), 1022 s ($\delta(CH_2)_{oop}$), 709 s ($\nu$(P−C)), 532 s cm^{-1} ($\delta$(P−Ph)). Anal. Calcd for $C_{40}H_{47}AuClPTi$: C, 57.25; H, 5.64. Found: C, 56.98; H, 5.53.

X-ray Structure Determination of 5e·2C_6H_6. Geometry and intensity data were collected with Mo Kα radiation at 203 K on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator ($\lambda = 0.7107$ Å). A summary of crystal data, data collection parameters, and convergence results is compiled in Table 4.

. After Lorentz and polarization corections, an empirical absorption correction based on azimuthal scans[47] was applied before averaging symmetry-related intensity data. The crystal clathrated two molecules of solvent (benzene) per asymmetric unit, which was partially lost. Thus, a relatively rapid data

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(47) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351−259.

collection had to be performed, and intensity data were corrected for the resulting decay on the basis of three regularly measured check reflections. The structures were solved by direct methods[48] and refined on structure factors with the local version of the SDP program suite.[49] In the full-matrix least-squares refinement, all non-hydrogen atoms were assigned anisotropic parameters. Hydrogen atoms were included as riding on the corresponding carbon atoms (C−H = 0.98 Å, U_{iso}(H) = 1.3U_{eq}C). Further details of the crystal structure determination are available on request from the Cambridge Crystallogarphic Data Center, on quoting the depository number CCDC-101161.

MO Calculations. Extended Hückel type[50] calculations were performed with the programm CACAO.[51] The geometry of the Cp_2Ti unit was idealized: Ti−Cp = 2.32 Å, C(Cp)−C(Cp) = 1.399 Å, C−H = 1.05 Å, Cp rings eclipsed with local C_{2v} symmetry. The PPh_3 group was replaced by PH_3, with P−H = 1.40 Å and angles of 109.4°. All other geometrical parameters were taken from the X-ray structure of **5e**.

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Supporting Information Available: Tables of positional parameters, displacement parameters, and bond lengths and angles for **5e** (12 pages). Ordering information is given on any current masthead page.

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[48] Sheldrick, G. M. SHELXS86, Program for Structure Solutions; University of Göttingen, Göttingen, Germany, 1986.

[49] Frenz, B. A. ENRAF-Nonius SDP, Version 5.0; Delft University: Delft, The Netherlands, 1990.

[50] (a) Hoffmann, R. *J. Chem. Phys.* **1963**, *19*, 1397−1412. (b) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 3489−3493.

[51] Mealli, C.; Proserpio, D. M. *J. Chem. Educ.* **1990**, *67*, 399−402.