Organometallics **1997,** *16,* 301−303

Formation of Palladium- and Platinum-Substituted Fulvenes by Cyclopentadienyl Activation in a Formal Insertion Reaction

Francisco M. Alías, Tomás R. Belderraín, Margarita Paneque,
Manuel L. Poveda,* and Ernesto Carmona*

Departamento de Química Inorgánica-Instituto de Investigaciones Químicas, Universidad de Sevilla-Consejo Superior de Investigaciones Científicas, C/Américo Vespuccio s/n, Isla de la Cartuja, 41092 Sevilla, Spain

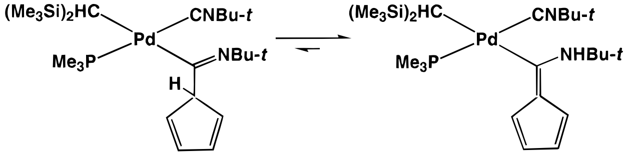
Pedro Valerga

Departamento de Ciencia de Materiales e Ingeniería Metalúrgica y Química Inorgánica, Facultad de Ciencias, Universidad de Cádiz, Apdo. 40, 11510 Puerto Real (Cádiz), Spain

Received September 27, 1996[⊗]

Summary: Stepwise, low-temperature reaction of {*Pd-*[*CH(SiMe$_3$)$_2$*](*PMe$_3$*)(*μ-Cl*)}$_2$ *with CNBu-t and NaCp′ (Cp′ = C$_5$H$_5$, C$_5$H$_4$Me) affords metal-substituted fulvenes of composition* {*Pd*[*C(NHBu-t)=C(C$_4$H$_3$R)*][*CH(SiMe$_3$)$_2$*]*-(CNBu-t)(PMe$_3$)*}, *of which the C$_5$H$_4$Me-derived complex* ***2b*** *(R = Me) has been characterized by X-ray crystallography. The formation of related complexes of Pt is also reported.*

Organic isocyanides, being isoelectronic with carbon monoxide, have a rich chemistry derived from their insertion into transition-metal−carbon bonds.[1] Both η^1- and η^2-iminoacyl structures, as well as a variety of polyimino-type products, have been reported to form.[1,2] Many different alkyl (or aryl) groups are able to migrate onto the isocyanide carbon. However, there seems to exist no report on insertion products derived from the ubiquitous cyclopentadienyl ligand, despite the ample precedent that now exists for the η^1-C_5H_5 coordination mode.[3] This is in contrast with the fact that examples of related formal insertions involving other unsaturated molecules into M−η^1-Cp bonds have been known for many years.[4] Herein we wish to describe the formation and structural characterization by spectroscopic techniques of the complexes {Pd[C(NHBu-*t*)=C(C$_4$H$_3$R)][CH(SiMe$_3$)$_2$](CNBu-*t*)(PMe$_3$)} (R = H (**2a**), Me (**2b**)). In a formal sense they originate from the migration of an η^1-Cp′ group (Cp′ = C$_5$H$_5$, C$_5$H$_4$Me) to a coordinated CNBu-*t* ligand, with subsequent tautomerism of the unobserved imine derivative to the more stable enamine form (structures **A** and **B**, respectively). Although a similar transformation has been proposed recently to explain the generation of the ketenimine Ph$_3$HC$_4$=C=NR in the reaction of [PdCl$_2$(CNR)$_2$] and KC$_5$HPh$_4$, no complex related to **2** could be detected.[5a]



A **B**

Interaction of [PdCl$_2$(cod)] (cod = 1,5-cyclooctadiene) with Mg[CH(SiMe$_3$)$_2$]Cl and 1 equiv of PMe$_3$ affords moderate yields of the chloride-bridged dimer {Pd[CH(SiMe$_3$)$_2$](PMe$_3$)(μ-Cl)}$_2$ (**1**). Upon stepwise addition of 2 equiv of CNBu-*t* and 1 equiv of NaCp to solutions of this compound, maintained at low temperatures, a complex transformation ensues that furnishes appreciable yields (*ca.* 45%) of compound **2a** (Scheme 1), together with {(η^5-C$_5$H$_5$)Pd[CH(SiMe$_3$)$_2$](PMe$_3$)} and other unidentified species. Analytical data indicate the incorporation of the Cp and the two CNBu-*t* ligands and are in accord with a formal insertion reaction (*i.e.* structure of type **A**), but spectroscopic studies[6] indicate that the complex exists in the tautomeric enamine form **B**. Thus, the IR spectrum contains a sharp, albeit weak, absorption at *ca.* 3322 cm^{-1}, indicative of the presence of a N−H bond, whose existence is further substantiated by the observation of a broad resonance at δ 6.94 in the ^{1}H NMR spectrum. The ^{13}C{^{1}H} NMR spectrum is

---

[⊗] Abstract published in *Advance ACS Abstracts*, January 1, 1997.

[1] (a) Bonati, F.; Minghetti, G. *Inorg. Chim. Acta* **1974,** *9,* 95. (b) Treichel, P. M. *Adv. Organomet. Chem.* **1973**, *11*, 21. (c) Singleton, E.; Oosthuizen, H. E. *Adv. Organomet. Chem.* **1983**, *22*, 209. (d) Yamamoto, Y.; Yamazaki, H. *Coord. Chem. Rev.* **1972**, *8*, 225. (e) Crociani, B. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum Press: New York, 1986; Vol. 1, Chapter 9, pp 553−638. (f) Durfee, L. D.; Rothwell, I. P. *Chem. Rev.* **1988**, *88*, 1059.

[2] (a) Otsuka, S.; Nakamura, A.; Yoshida, T.; Naruto, M.; Ataka, K. *J. Am. Chem. Soc.* **1973**, *95*, 3180. (b) Yamamoto, Y.; Yamazaki, H. *Inorg. Chem.* **1974,** *13,* 438. (c) Aoki, K.; Yamamoto, Y. *Inorg. Chem.* **1976**, *15*, 48. (d) Bellachioma, G.; Gardaci, G.; Zanazzi, P. *Inorg. Chem.* **1987**, *26*, 84. (e) Maitlis, P. M.; Espinet, P.; Russell, M. J. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 6, p 279.

[3] O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307. For a very recent example see: Cross, R. J.; Farrugia, L. J.; Kuma, K. E. A. *J. Organomet. Chem.* **1994**, *471*, 273.

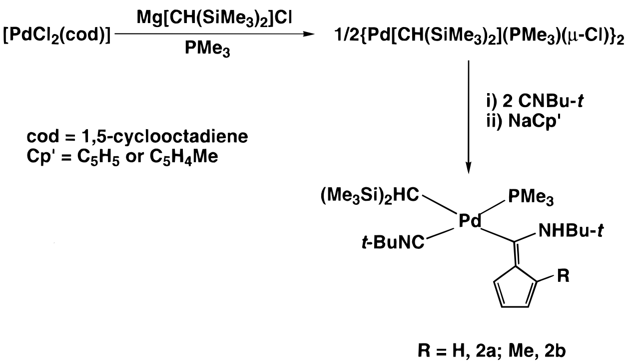
[4] (a) Casey, C. P.; O'Connor, J. M.; Haller, K. J. *J. Am. Chem. Soc.* **1985**, *107*, 1241. (b) Anderson, G. K. *Organometallics* **1986**, *5*, 1903. (c) O'Hare, D. *Organometallics* **1987**, *6*, 1766. (d) Hill, M. N. S.; Johnson, B. F. G.; Keating, T.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1975**, 1197.

[5] (a) Tanese, T.; Fukushima, T.; Nomura, T.; Yamamoto, Y. *Inorg. Chem.* **1994**, *33*, 32. (b) Onitsuka, K.; Ogawa, H.; Joh, T.; Takahashi, S.; Yamamoto, Y.; Yamazaki, H. *J. Chem. Soc., Dalton Trans.* **1991**, 1531. (c) Veya, P.; Floriani, C.; Chiesa-Villa, A.; Rizzoli, C. *Organometallics* **1993**, *12*, 4899.

[6] Selected spectroscopic and analytical data for **2a**: ^{1}H NMR (C$_6$D$_6$, 25 °C) δ −0.67 (d, $^3J_{HP}$ = 14.5 Hz, 1H, C*H*(SiMe$_3$)$_2$), 0.35 (s, 9H, SiMe$_3$), 0.50 (s, 9H, SiMe$_3$), 0.89 (s, 9H, CNCMe$_3$), 0.95 (d, $^2J_{HP}$ = 9.4 Hz, 9H, PMe$_3$), 1.29 (s, 9H, NHC*Me$_3$*), 6.66 (m, 1H, CH$_{fulv}$), 6.80 (m, 2H, CH$_{fulv}$), 6.95 (br s, 1H, NH), 7.20 (m, 1H, C*H*$_{fulv}$); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C) δ 0.5 (d, $^2J_{CP}$ = 5 Hz, *C*H(SiMe$_3$)$_2$), 15.1 (d, $^1J_{CP}$ = 32 Hz, PMe$_3$), 102.2, 114.7, 120.4, 123.6 (s, CH$_{fulv}$), 129.2 (s, C=*C*C$_4$H$_4$), 139.1 (d, $^2J_{CP}$ = 154 Hz, *C*NBu-*t*), 206.0 (d, $^2J_{CP}$ = 9 Hz, *C*=CC$_4$H$_4$); IR (Nujol, cm^{-1}) ν(NH) 3322 (w). Anal. Calcd for C$_{25}$H$_{51}$N$_2$PSi$_2$Pd: C, 52.4; H, 9.0; N, 4.9. Found: C, 52.0; H, 8.9; N, 4.6.

S0276-7333(96)00826-6 CCC: $14.00

Scheme 1



particularly informative. As expected, the methyne carbon of the alkyl group resonates at high field (δ 0.5, d, $^2J_{CP} = 5$ Hz), while the Pd−*C*NBu-*t* carbon gives rise to a doublet at δ 139.1. The strong $^{13}C-^{31}P$ coupling of 154 Hz found for this carbon nucleus is typical of a mutual *trans* disposition of the CNBu-*t* and PMe_3 ligands. The Pd-bound ^{13}C atom of the enamine moiety appears at low field (δ 206, d, $^2J_{CP} = 9$ Hz), whereas the resonances of the five nonequivalent carbon atoms of the original Cp fragment cluster between 102 and 129 ppm.

Crystals of **2a** were found unsuitable for X-ray studies, but the structure of the analogous C_5H_4Me derivative **2b**, prepared by a similar procedure (Scheme 1), could be determined by X-ray diffraction methods.[7] As can be observed in Figure 1, the Pd center is in a distorted-square-planar coordination environment, with the terminal isocyanide carbon atom C(8) presenting the largest deviation (0.28 Å) from the least-squares plane defined by Pd, P, C(1), C(8), and C(13). The fulvene moiety is planar and is almost perpendicular to the Pd coordination plane (dihedral angle of 80.77°), possibly to minimize adverse steric interactions. The Pd−C(1) bond of 2.17(1) Å is somewhat longer than Pd−C(13) at 2.09(1) Å, due to differences in the hybridization at carbon. The latter length is in the range normally found for the Pd−C(sp^2) bonds.[5b,c] The remaining bond distances within the fulvene unit are similar to those found in $H_4C_4C{=}C(H)NMe_2$.[8]

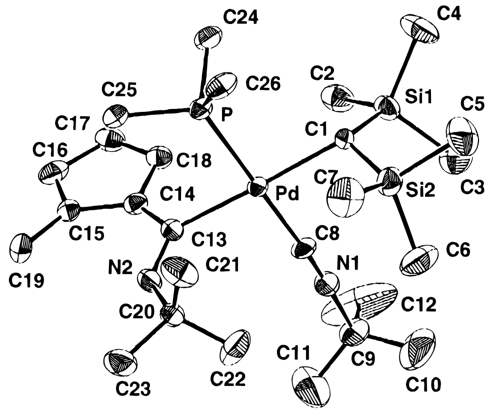


Figure 1. Molecular structure of complex **2b** showing the atom-labeling scheme. Hydrogen atoms have been omitted for clarity. ORTEP ellipsoids represent 30% probability. Selected bond distances (Å) and angles (deg) with esd's in parentheses: Pd−P, 2.295(3); Pd−C(1), 2.17(1); Pd−C(8), 1.99(1); Pd−C(13), 2.09(1); P−Pd−C(1), 89.0(3); P−Pd−C(8), 170.9(3); P−Pd−C(13), 89.0(3); C(1)−Pd−C(8), 170.9(3); C(1)−Pd−C(13), 177.8(4); C(8)−Pd−C(13), 89.1(4).

Transition-metal fulvenes are known,[9] and some cobaltafulvene complexes that contain $Co{=}CCH{=}CH{-}CH{=}CH$ have been described.[10] We are, however, unaware of the existence of compounds having a structure of the kind found for **2**. Casey and co-workers have disclosed a similar transformation during the course of the reaction of $[(\eta^1\text{-}C_5H_5)Re(NO)(CH_3)(CO)(PMe_3)_2]$ with high concentrations of PMe_3. This gave the structurally characterized cyclopentadienylidene ketene species $\{(PMe_3)_3(NO)Re[C(O){=}C(C_4H_4)]\}$, in a process that involves formally the insertion of CO into a Re−η^1-C_5H_5 bond.[4a]

Work aimed at clarifying the mechanistic aspects of the conversion of complex **1** into **2a** and **2b** is presently underway. However, in view of literature precedent[1,11] it is reasonable to assume the intermediacy of a cationic alkyl bis(isocyanide) species, $\{Pd[CH(SiMe_3)_2](CNBu\text{-}t)_2(PMe_3)\}Cl$. Efforts directed toward the isolation of such species have proved unsuccessful, but nonetheless the platinum analogue $\{Pt[CH(SiMe_3)_2](CNBu\text{-}t)_2(PMe_3)\}Cl$ has been obtained (Scheme 2) and shown to

---

(7) Selected spectroscopic and crystallographic data for **2b**: ^1H NMR (C_6D_6, 25 °C) δ −0.69 (d, $^3J_{HP} = 14.2$ Hz, 1H, C*H*(SiMe$_3$)$_2$), 0.38 (s, 9H, SiMe$_3$), 0.51 (s, 9H, SiMe$_3$), 0.88 (s, 9H, CNCMe$_3$), 0.95 (d, $^2J_{HP} = 9.6$ Hz, 9H, PMe$_3$), 1.38 (s, 9H, NHC*Me$_3$*), 2.59 (s, 3H, *Me*CC$_4$H$_3$), 6.47 (m, $^3J_{HH} = 2.6$, $^4J_{HH} = 2.2$, $^4J_{HH(Me)} = 1.1$ Hz, 1H, CH$_{fulv}$), 6.66 (dd, $^3J_{HH} = 4.4$, $^3J_{HH} = 2.6$ Hz, 1H, CH$_{fulv}$), 6.99 (br s, 1H, NH), 7.16 (dd, $^3J_{HH} = 4.4$, $^4J_{HH} = 2.2$ Hz, 1H, CH$_{fulv}$); $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C) δ −0.3 (d, $^2J_{CP} = 6$ Hz, *C*H(SiMe$_3$)$_2$), 14.5 (d, $^1J_{CP} = 31$ Hz, PMe$_3$), 19.0 (s, *Me*CC$_4$H$_3$), 115.0, 120.0, 124.6 (s, CH$_{fulv}$), 117.1 (s, C=C*C*(Me)C$_3$H$_3$), 129.0 (s, C=*C*C(Me)C$_3$H$_3$), 140.0 (d, $^2J_{CP} = 159$ Hz, *C*NBu-*t*), 200.6 (d, $^2J_{CP} = 8$ Hz, *C*=CC(Me)C$_3$H$_3$); IR (Nujol, cm^{-1}) ν(NH) 3326 (w). The crystal selected for the X-ray study contained half a molecule of 1,2-dimethoxyethane of crystallization per asymmetric unit. Crystallographic data for $\{Pd[C(NHBu\text{-}t){=}C(C_4H_3Me)][CH(SiMe_3)_2](CNBu\text{-}t)(PMe_3)\}$: $C_{28}H_{58}N_2POPdSi_2$, fw 632.32, triclinic, $P\bar{1}$ (No. 2), $a = 16.254(5)$ Å, $b = 11.101(2)$ Å, $c = 11.081(2)$ Å, $\alpha = 90.60(2)°$, $\beta = 70.52(2)°$, $\gamma = 83.78(2)°$, $V = 1872(2)$ Å^3, $Z = 2$, $D_c = 1.122$ g cm^{-3}, λ(Mo Kα) = 0.710 69 Å, μ(Mo Kα) = 6.12 cm^{-1}, $F(000) = 674$, $T = 290$ K, $R = 0.051$ for 2654 observed reflections ($I > 3\sigma(I)$), $R_w = 0.055$ (weighted $w = \sigma_F^{-2}$). A yellow plate having approximate dimensions of 0.28 × 0.15 × 0.30 mm was mounted on a glass fiber and transferred to an Rigaku AFC6S single-crystal diffractometer. The cell parameters were obtained from the settings of 25 reflections in the range 11.61 < 26 < 17.73°. The data were collected in the interval 5 < 2 < 45°, using the $\omega-2\theta$ scan method at a speed of 8°/min. The standard reflections were intensity-controlled for decay correction (the final decay was 16%). Absorption correction (ψ-scan method and transmission factors in the range 0.93−1.00) and Lorentz and polarization corrections were also applied. The structure was solved by the Patterson method and phase expansion and refinement of the remainder of the structure. All non-hydrogen atoms in the complex molecule were anisotropically refined; the carbon and oxygen atoms in the solvate were isotropically refined by full-matrix, least-squares methods. Approximately half of the hydrogen atoms were localized in difference Fourier maps, and the rest have been placed at calculated positions. Refinements concluded with $R = 0.051$, $R_w = 0.055$, and goodness of fit 1.24. Scattering factors were taken from those included in the TEXSAN system,[16] running on a DEC VAX 3520 at the Servicios Centralizados de Ciencia y Tecnología, Universidad de Cádiz.

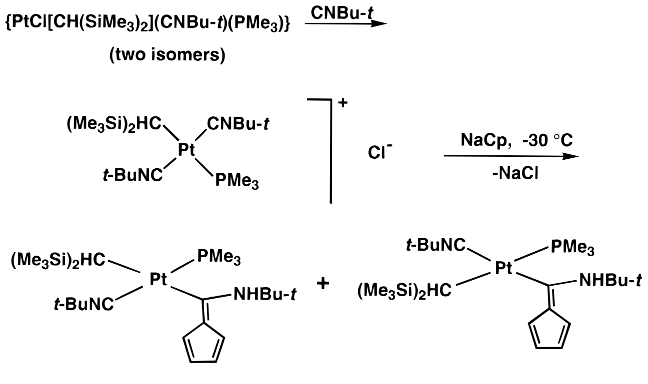
(8) Ammon, H. L. *Acta Crystallogr. Sect. B* **1974**, *30*, 1731.

(9) (a) Bandy, J. A.; Mtetwa, V. S. B.; Prout, K.; Green, J. C.; Davies, C. E.; Green, M. L. H.; Hazel, N. J.; Izquierdo, A.; Martin-Polo, J. J. *J. Chem. Soc., Dalton Trans.* **1985**, 2037. (b) Schock, L. E.; Brock, C. P.; Marks, T. J. *Organometallics* **1987**, *6*, 237. (c) Glueck, D. S.; Bergman, R. G. *Organometallics* **1990**, *9*, 2862. (d) McDade, C.; Green, J. C.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1629. (e) Gusev, O. V.; Sergeev, S.; Saez, I. M.; Maitlis, P. M. *Organometallics* **1994**, *13*, 2059. (f) Blake, A. J.; Dyson, P.; Johnson, B. F. G.; Reed, D.; Shephard, D. S. *J. Chem. Soc., Chem. Commun.* **1994**, 1347. (g) Kerber, R. C.; Ehntholt, D. J. *Synthesis* **1970**, *9*, 449.

(10) For some recent examples see: Wadepohl, H. *Comments Inorg. Chem.* **1994,** *15*, 369.

(11) (a) Onitsuka, K.; Ogawa, H.; Joh, T.; Takahashi, S.; Yamamoto, Y.; Yamazaki, H. *J. Chem. Soc., Dalton Trans.* **1991**, 1531. (b) Delis, J. G. P.; Aubel, P. G.; van Leeuwen, P. W. N. M.; Vrieze, K.; Veldman, N.; Spek, A. L. *J. Chem. Soc., Chem. Commun.* **1995**, 2233.

Scheme 2



3 (two isomers)

interconvert into the corresponding fulvene {Pt[C(NHBu-*t*)═C(C_4H_4)][CH($SiMe_3$)$_2$](CNBu-*t*)(PMe_3)} (**3**) by reaction with NaCp.[12] As depicted in Scheme 2, compound **3** is formed as a mixture of two isomers that have *cis* phosphine and fulvene ligands. A third, so far unidentified product has also been detected. Our data do not allow us to distinguish between a concerted Cp migration in a M$-\eta^1$-C_5H_5 intermediate and a direct nucleophilic attack on the isocyanide carbon in the reactions that give the metal-substituted fulvenes.

The adoption by **2** and **3** of the enamine-type structure **B**, as opposed to the imine formulation **A**, deserves some comment. Complexes **2** and **3** display high thermal stability and can be recovered unaltered after heating their solutions at temperatures near 80 °C. Since it is probable that the reactions summarized in Schemes 1 and 2 yield initially products of a straightforward coupling reaction, *i.e.* imine structures, it would appear reasonable that formation of the fulvene structures **2** and **3** occurs under thermodynamic control. The higher stability encountered for the enamine forms is unusual in transition-metal chemistry, where the imine formulation is predominant,[1,13] and it is clearly at odds with the situation normally observed in the chemistry of their organic counterparts. For these, enamines having a hydrogen atom on the nitrogen are usually unstable with respect to the corresponding imines.[14] In our case, the adoption of the enamine form by compounds **2** and **3** is doubtless driven by the tendency to fulvene formation. This has ample precedent in organic fulvenes, where, for example, 6-hydroxyfulvene is preferred over the corresponding nonfulvenoid keto form.[15]

Acknowledgment. We gratefully acknowledge financial support from the Dirección General de Investigación Científica y Técnica (Proyectos PB93-0921 and PB94-1445) and the Junta de Andalucía. T.R.B. and F.M.A. thank the Spanish Ministerio de Educación y Ciencia for research grants. Thanks are also due to the University of Seville for the use of its analytical and NMR facilities.

Supporting Information Available: Text giving experimental details for the synthesis of complexes **1**−**3** and tables of crystal and refinement data, bond lengths and angles, atomic coordinates, and thermal parameters for **2b** (10 pages). Ordering information is given on any current masthead page.

OM9608263

---

[12] Complex **3** can be generated from {Pt[CH($SiMe_3$)$_2$]Cl(CNBu-*t*)(PMe_3)} by successive low-temperature (−30 °C) reactions with CNBu-*t* and NaCp or from isolated samples of *trans*-{Pt[CH($SiMe_3$)$_2$](PMe_3)(CNBu-*t*)$_2$}Cl following treatment with NaCp at −30 °C. Selected spectroscopic and analytical data for the major isomer: ^{1}H NMR (300 MHz, CD_3COCD_3, −50 °C) δ −0.18 (s, 9H, $SiMe_3$, 0.08 (s, 9H, $SiMe_3$), 1.35 (d, $^2J_{HP} = 9.9$ Hz, 9H, PMe_3), 1.50 (s, 9H, $CNCMe_3$), 1.63 (s, 9H, NHC*Me*$_3$), 5.70, 5.74, 6.14, 6.60 (m, 1H each, CH_{fulv}), 7.61 (s, 1H, $^3J_{HPt} = 105$ Hz, NH); ^{31}P{^{1}H} NMR (81 MHz, CD_3COCD_3, −50 °C) δ −24.2 ($^1J_{PPt} = 1970$ Hz); ^{13}C{^{1}H} NMR (75 MHz, CD_3COCD_3, −50 °C) δ −3.02 (d, $^2J_{CP} = 69$ Hz, *C*H($SiMe_3$)$_2$), 5.6, 6.5 (s, CH(Si*Me*$_3$)$_2$), 13.9 (d, $^1J_{CP} = 34$, $^2J_{CPt} = 30$ Hz, PMe_3), 29.9 (s, CNC*Me*$_3$), 31.4 (s, NHC*Me*$_3$), 54.3 (s, NH*C*Me$_3$), 59.1 (s, *C*NCMe$_3$), 105.1, 114.0, 115.7, 124.8 (s, CH_{fulv}), 128.4 (s, C═*C*C$_4$H$_4$), 193.9 (d, $^2J_{CP} = 11$ Hz, Pt−*C*═CC$_4$H$_4$); IR (Nujol, cm^{-1}) ν(NH) 3350 (w). Anal. Calcd for $C_{25}H_{51}N_2PSi_2Pt$: C, 45.39; H, 7.71; N, 4.23. Found: C, 45.45; H, 7.8; N, 3.9.

[13] Cámpora, J.; Hudson, S. A.; Carmona, E. *Organometallics* **1995**, *14*, 2151.

[14] (a) Lammertsma, K.; Prasad, B. V. *J. Am. Chem. Soc.* **1994**, *116*, 642. (b) De Jeso, B.; Pommier, J. C. *J. Chem. Soc., Chem. Commun.* **1977**, 565.

[15] Bergman, E. D. *Chem. Rev.* **1968**, *68*, 41.

[16] TEXSAN-TEXRAY Structure Analysis Package, Molecular Structure Corp., 1985.