Formation of Palladium- and Platinum-Substituted Fulvenes by Activation of a Cyclopentadienyl or Indenyl Ligand

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 Vespucio 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 July 29, 1998

The stepwise, low-temperature reaction of $\{Pd[CH(SiMe_3)_2](\mu\text{-}Cl)(PMe_3)\}_2$ (**1**) with CNBu-*t* and NaCp′ (Cp′ = C_5H_5, C_5H_4Me) or LiInd (Ind = C_9H_7) affords metal-substituted fulvenes of composition $Pd[C(NHBu\text{-}t)=C(C_4H_3R)][CH(SiMe_3)_2](CNBu\text{-}t)(PMe_3)$ (R = H, Me) and $Pd[C(NHBu\text{-}t)=C(C_8H_6)][CH(SiMe_3)_2](CNBu\text{-}t)(PMe_3)$, of which the C_5H_4Me-derived complex **5a** has been characterized by X-ray crystallography. The mononuclear species $Pd[CH(SiMe_3)_2]Cl(CNBu\text{-}t)(PMe_3)$ (**2**) has been isolated as an intermediate of this reaction. An alternative synthesis of the palladabenzofulvene complex **6** involves the reaction of the 16 electron indenyl derivative (η^3-Ind)$Pd[CH(SiMe_3)_2](PMe_3)$ (**7**) with 2 equiv of CNBu-*t*. In this case an η^1-indenyl intermediate of composition (η^1-Ind)$Pd[CH(SiMe_3)_2](CNBu\text{-}t)(PMe_3)$ (**8**) can be observed by low-temperature NMR spectroscopy. The complex $Pt[CH(SiMe_3)_2]Cl(CNBu\text{-}t)(PMe_3)$ (**12**) has been synthesized by the comproportionation reaction of $Pt[CH(SiMe_3)_2]Cl(PMe_3)_2$ (**10**) and $Pt[CH(SiMe_3)_2]Cl(CNBu\text{-}t)_2$ (**11**), in the presence of catalytic amounts of CNBu-*t*. Complex **12** reacts with CNBu-*t* and NaCp to give first the cationic species $\{Pt[CH(SiMe_3)_2](CNBu\text{-}t)_2(PMe_3)\}Cl$ (**13**) and then a mixture of platinafulvene isomers related to the above-mentioned Pd complexes. The fluxionality of these metallafulvene derivatives and the mechanism of their formation are discussed.

Introduction

Organic isocyanides have a rich chemistry derived from their migratory insertion into transition metal−carbon bonds.[1,2] Both η^1- and η^2-iminoacyl structures have been reported to form along with a variety of polyimino-type products derived from multiple insertion reactions.[1,2] Many different alkyl (or aryl) groups are able to migrate onto the isocyanide carbon. However, there seems to be no report on complexes that proceed from the migratory insertion of the ubiquitous cyclopentadienyl ligand, despite the ample precedent that now exists for its monohapto coordination mode.[3] This contrasts 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] For instance, Casey and co-workers have disclosed a CO migratory insertion of this kind during the course of the reaction of (η^1-C_5H_5)$Re(CH_3)(CO)(NO)(PMe_3)_2$ with a large excess of PMe_3. This gave the structurally characterized cyclopentadienylidene ketene species $Re[C(O)=C(C_4H_4)](NO)(PMe_3)_3$.[4a]

Recently we have reported the synthesis of the η^2-iminoacyl complex Ni[η^2-C(NBu-*t*)$CH(SiMe_3)_2$]$Cl(PMe_3)$, the first nickel compound of this type to be structurally authenticated by X-ray crystallography. This compound is generated by migratory insertion of CNBu-*t* into the Ni−C bond of the dimeric alkyl $\{Ni[CH(SiMe_3)_2](\mu\text{-}Cl)(PMe_3)\}_2$.[5] During the course of these studies we

(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, 1982; Vol. 6, p 279.

(3) (a) O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307. (b) For a 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.

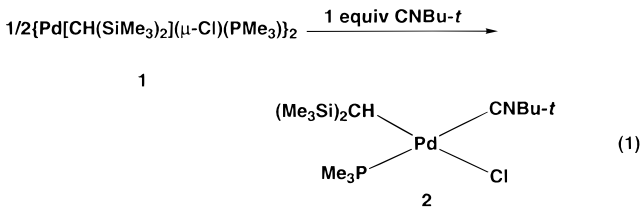
(5) (a) Belderrain, T. R.; Paneque, M.; Poveda, M. L.; Sernau, V.; Carmona, E.; Gutiérrez, E.; Monge, A. *Polyhedron* **1995**, *14*, 323. (b) Belderrain, T. R.; Paneque, M.; Poveda, M. L.; Sernau, V.; Carmona, E.; Gutiérrez, E.; Monge, A. *Polyhedron* **1996**, *15*, 3501.

10.1021/om9806500 CCC: $15.00
Publication on Web 11/20/1998

became interested in the related chemistry of Pd− and Pt−alkyl complexes that contain the bulky hydrocarbyl unit $CH(SiMe_3)_2$. In this contribution we wish to report the results of the reactions that involve the sequential use of *tert*-butylisocyanide and cyclopentadienyl-type ligands. As discussed below, the products of these transformations have composition M[C(NHBu-*t*)═C-(C_4H_3R)][$CH(SiMe_3)_2$](CNBu-*t*)(PMe_3) (M = Pd, Pt; R = H, Me) and Pd[C(NHBu-*t*)═C(C_8H_6)][$CH(SiMe_3)_2$](CNBu-*t*)(PMe_3) and exhibit metallafulvene structures. At least in a formal sense these complexes can be thought of as deriving from the migratory insertion of the organic isocyanide into a M−η^1-Cp or M−η^1-Ind bond (Ind = C_9H_7), followed by tautomerization of the resulting iminoacyl functionality. Part of this work has appeared in a preliminary form.[6]

Results

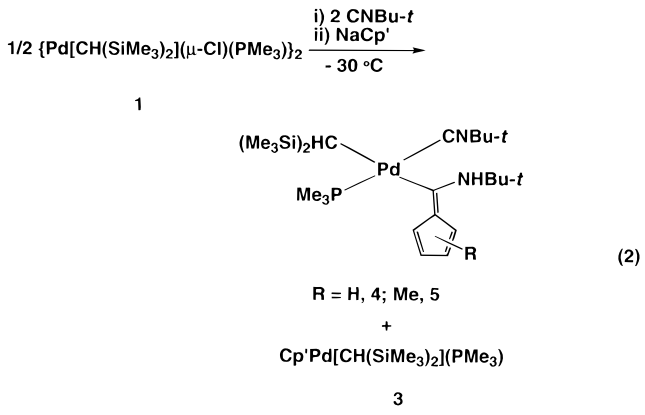
Synthesis and Characterization of Palladafulvene Complexes. The reaction of 1 equiv of CNBu-*t* with the recently described dimer {Pd[$CH(SiMe_3)_2$](μ-Cl)(PMe_3)}$_2$ (**1**)[7] cleanly and stereospecifically affords the new isocyanide adduct Pd[$CH(SiMe_3)_2$]Cl(CNBu-*t*)-(PMe_3) (**2**), which has been fully characterized by spectroscopy (eq 1).



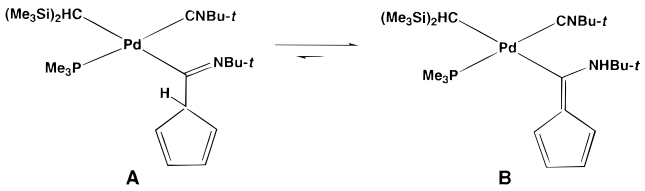
(1)

At variance with the results found in the analogous Ni system,[5] no insertion of the isocyanide into the Pd−alkyl bond takes place under these conditions. However, the formation of **2** is not an unexpected observation, as neutral Pd(II)−alkyl complexes which contain isocyanide ligands are rather inert toward this rearrangement. In those cases where this insertion reaction is facile the intermediate isocyanide adduct is usually sufficiently long-lived to be observed.[1e,8]

When an excess (≥2 equiv) of CNBu-*t* is added to a cold solution (−30 °C) of **1** in Et_2O a white precipitate forms. Due to a complex decomposition reaction, no clean products can be isolated after work up, but treatment of the above suspension with 1 equiv of NaCp, also at −30 °C, furnishes, among other unidentified compounds, the palladafulvene derivative Pd[C(NHBu-*t*)═C(C_4H_4)][$CH(SiMe_3)_2$](CNBu-*t*)(PMe_3) (**4**) in 45% yield (eq 2). The already described complex (η^5-C_5H_5)-Pd[$CH(SiMe_3)_2$](PMe_3) (**3**) is also generated in this reaction and can be separated from **4** by fractional crystallization.[7] Analytical data and spectroscopic studies indicate the incorporation of a Cp and two CNBu-*t* ligands and are in accord with **4** having formulation **B**, i.e. the tautomeric enamine form of the imonoacyl structure **A**, that would result from the formal insertion



(2)



of CNBu-*t* into a Pd−η^1-Cp bond. 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 ^1H NMR spectrum. The $^{13}C\{^1H\}$ NMR spectrum is particularly informative. The mutually trans arrangement of the CNBu-*t* and PMe_3 ligands is indicated by the strong $^{13}C-^{31}P$ coupling of 154 Hz found for the Pd-*C*NBu-*t* nucleus (δ 139.1). The Pd-bound ^{13}C atom of the enamine moiety appears at low field (δ 206.0, d, $^2J_{CP}$ = 5 Hz), whereas the resonances of the five nonequivalent carbon atoms of the original Cp fragment cluster between 102 and 129 ppm. Rotation of the C_5 ring around the C═C double bond is therefore slow in the NMR time scale at 25 °C, in good agreement with the behavior of related organic[9] and organometallic[10] systems.

The use of methylcyclopentadienyl anion allows for the formation of the corresponding substituted fulvene complex **5** (eq 2), which because of the presence of the methyl group in the Cp ring is produced as a mixture of stereoisomers. The $^{31}P\{^1H\}$ NMR spectrum of the crude of the reaction shows the existence of three, out of the four possible isomers **5a**−**d** depicted in Scheme 1, in a ratio of 6:5:3. Pure samples of **5a** can be isolated by fractional crystallization from cold petroleum ether solutions and its structure unambiguously assigned by means of NOEDIFF experiments (Scheme 1). The most significant NOEs are (i) H_c (δ 6.47) and the NH proton (δ 6.99) with the protons of the methyl group of the C_5H_4Me ligand; (ii) H_b (δ 6.66) with H_c and H_a (δ 7.16). For the other isomers proton chemical shift and coupling constant data cannot either be confidently used for

(6) Alías, F. M.; Belderrain, T. R.; Paneque, M.; Poveda, M. L.; Carmona, E.; Valerga, P. *Organometallics* **1997**, *16*, 301.
(7) Alías, F. M.; Belderrain, T. R.; Carmona, E.; Graiff, C.; Paneque, M.; Tiripicchio, A. *J. Organomet. Chem.*, in press.
(8) (a) Otsuka, S.; Nakamura, A.; Yoshida, T. *J. Am. Chem. Soc.* **1969**, *91*, 7196. (b) Yamamoto, Y.; Yamazaki, H.; Hagihara, N. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 532. (c) Yamamoto, Y.; Yamazaki, H.; Hagihara, N. *J. Organomet. Chem.* **1969**, *10*, 189. (d) Maitlis, P. M.; Espinet, P.; Russell, M. J. H. In *Comprehesive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: London, 1982; Vol. 6, Chapter 38.4.
(9) Ammon, H. L. *Acta Crystallogr., Sect. B* **1974**, *30*, 1731.
(10) Legzdings, P.; Lumb, S. A.; Young, V. G., Jr. *Organometallics* **1998**, *17*, 854.

Scheme 1

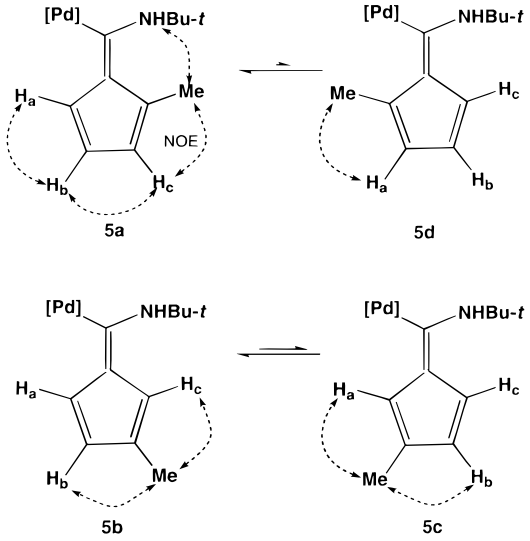


Table 1. Selected Bond Distances (Å) and Angles (deg) for 5a

Pd−P	2.295(3)	P−Pd−C(1)	89.3(2)
Pd−C(1)	2.17(1)	P−Pd−C(8)	170.9(3)
Pd−C(8)	1.99(1)	P−Pd−C(13)	89.0(3)
Pd−C(13)	2.09(1)	C(1)−Pd−C(8)	92.3(4)
C(13)−C(14)	1.37(1)	C(1)−Pd−C(13)	177.8(4)
C(13)−N(2)	1.35(1)	C(8)−Pd−C(13)	89.1(4)

unequivocal structural identification but as for **5a** NOEDIFF experiments prove conclusive. Thus, irradiation of the resonance corresponding to the ring methyl group of the other two fulvene species produces NOE effects with two neighboring protons. This implies that these species are **5b** and **5c**, for the case of **5d** only one NOE effect (with H_a) would have been observed (Scheme 1). Finally we have also made use in this analysis of the closer similarity expected for the chemical shifts of H_a and H_b in isomers **5a** and **5b** in comparison with **5c**. The ratio in which these complexes appear to coexist is **5a**/**5b**/**5c** = 5:6:3, and while the **5b**/**5c** proportion is probably thermodynamic in nature because of the effective rotation around the C═C bond in the laboratory time scale,[9,10] the fraction of **5a** may reflect the kinetic distribution of the reaction.

The structure of the **5a** isomer has been confirmed by X-ray diffraction methods. Selected bond distances and angles can be found in Table 1. 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.[11] The remaining bond distances within the fulvene unit, particularly those of C(13)−C(14) and C(13)−N(2) bonds (1.37(1) and 1.35(1) Å, respectively), are similar to those found in H_4C_4C═C(H)NMe_2.[9]

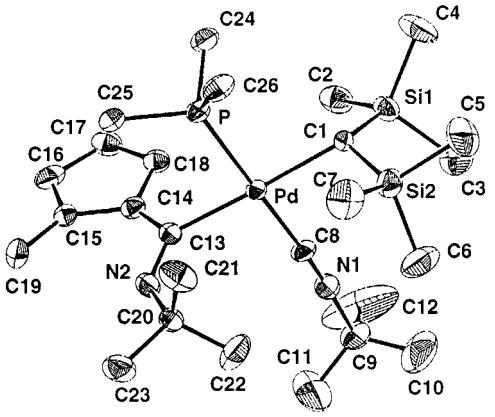
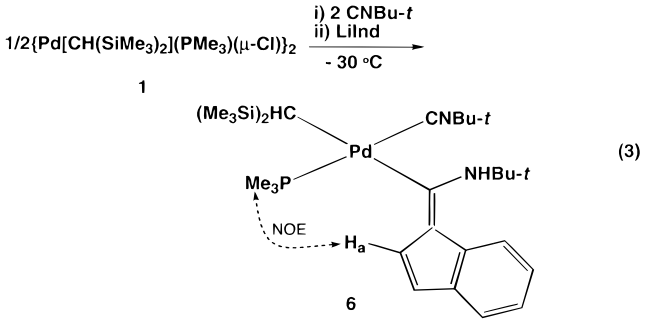


Figure 1. Molecular structure of complex **5a** showing the atom labeling scheme. Hydrogen atoms have been omitted for clarity. ORTEP ellipsoids represent 30% probability.

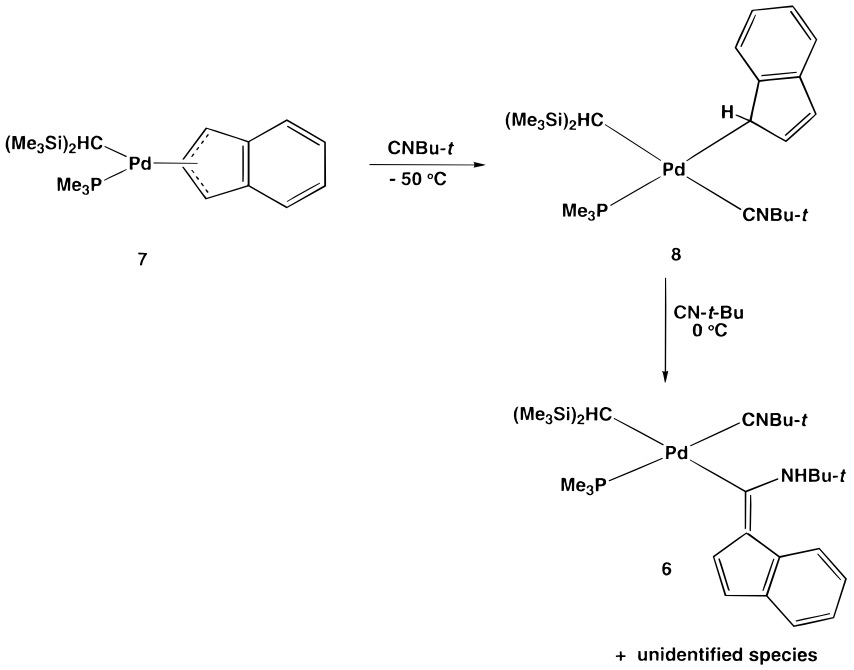
A similar transformation is observed when LiInd is used instead of a cyclopentadienyl reagent. Upon stepwise addition of 2 equiv of CNBu-*t* and 1 equiv of LiInd to solutions of **2** at low temperatures the benzoannulated fulvene derivative Pd[C(NHBu-*t*)═C(C_8H_6)]-[CH($SiMe_3$)$_2$](CNBu-*t*)(PMe_3) (**6**) is formed in a ca. 40% yield (eq 3). The presence of an absorption at 3390 cm^{-1} in the IR spectrum, and an associated broad singlet at δ 7.27 in the ^{1}H NMR spectrum are indicative of the existence of a NH group. Additionally the analysis of the resonances found in both the ^{1}H and the $^{13}C\{^1H\}$ NMR spectra reveal the presence of a fulvene unit (in this case with a fused benzene ring) bonded to the metal center through the *exo* carbon (δ 196.7). The ligand disposition around the metal center is easily deduced from the ^{1}H and $^{13}C\{^1H\}$ NMR spectra as has already been detailed for **4** and **5**. Two possible stereoisomers ("rotamers") are to be expected depending on the relative position of the benzene ring with respect to the amino group, but just one is observed by NMR spectroscopy. The presence of a NOE effect on H_a upon saturation of the PMe_3 protons clearly shows that the favored stereoisomer is the one depicted in eq 3.



Interestingly, the fulvene derivative **6** can be prepared by reaction of the indenyl complex (η^3-Ind)Pd[CH-($SiMe_3$)$_2$](PMe_3) (**7**)[7] with 2 equiv of CNBu-*t*. In an attempt to gain mechanistic information this transformation has been monitored by low temperature NMR spectroscopy. Only 1 equiv of the isocyanide reacts initially, and an η^1-indenyl species **8** is cleanly formed at −50 °C (Scheme 2). Particularly informative from a structural point of view is the presence of a doublet in

(11) (a) Onitsuka, K.; Ogawa, H.; Joh, T.; Takahashi, S.; Yamamoto, Y.; Yamazaki, H. *J. Chem. Soc., Dalton Trans.* **1991**, 1531. (b) Veya, P.; Floriani, C.; Chiesa-Villa, A.; Rizzoli, C. *Organometallics* **1993**, *12*, 4899.

Scheme 2



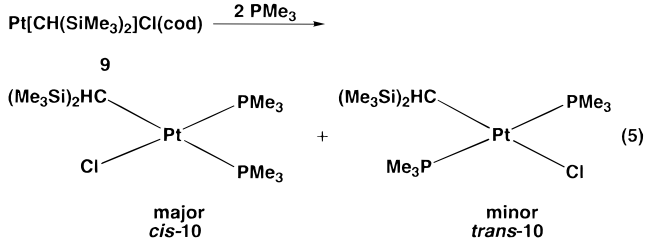
the $^{13}C\{^1H\}$ NMR spectrum at δ 48.15 ($^2J_{CP}$ = 69 Hz). This is assigned to the methyne group of the Pd−*C*H-(ind) moiety and the strong $^{13}C-^{31}P$ coupling is indicative of the trans disposition of the η^1-indenyl ligand with respect to the PMe_3 group. The spectroscopic data recorded for **8** are similar to those found for other transition metal η^1-indenyl complexes that have been reported in the literature.[12] The clean formation of intermediate **8** implies that the isocyanide attacks selectively the Pd atom at one of the pseudoallylic positions of **7**, that which is trans with respect to the $CH(SiMe_3)_2$ group (Scheme 2).

If the reaction temperature is allowed to reach 0 °C, **8** gradually disappears and the resonances corresponding to the indenylfulvene species **6** (among those of other species) concomitantly grow up in the ^1H NMR spectrum of the reaction mixture.

Synthesis of Pt[CH(SiMe$_3$)$_2$]Cl(CNBu-*t*)(PMe$_3$) (12). To gain further information about the mechanism of formation of these palladafulvene complexes and with the expectation of isolating reaction intermediates we decided to study the related Pt system. As an entry to this chemistry the complex Pt[$CH(SiMe_3)_2$]Cl(cod) (**9**) (cod = 1,5-cyclooctadiene) was prepared by the procedure described[13] by Young and co-workers for the synthesis of related alkyls (eq 4).

$$PtCl_2(cod) \xrightarrow{Mg[CH(SiMe_3)_2]Cl} \underset{\mathbf{9}}{Pt[CH(SiMe_3)_2]Cl(cod)} \qquad (4)$$

All the efforts directed to obtain a dimeric Pt complex similar to **1** by addition of 1 equiv of PMe_3 to solutions of **9** were unsuccessful, and equimolecular mixtures of unreacted starting material and the monomeric compound Pt[$CH(SiMe_3)_2$]Cl(PMe_3)$_2$ (**10**) were always obtained. In accord with this result, the reaction of **9** with 2 equiv of PMe_3 cleanly gives the bis(phophine) adduct **10** (eq 5) which is generated as a kinetic mixture of the



cis and trans isomers in a 3:1 ratio. The former, i.e., the *cis*-**10** isomer can be readily isolated by fractional crystallization from petroleum ether/Et_2O mixtures. The analysis of its $^{31}P\{^1H\}$ NMR spectrum is straightforward[14] and merits no further comment but for the *trans* isomer the corresponding spectrum is somewhat more complicated due to the restricted rotation around Pt−$CH(SiMe_3)_2$ bond. This behavior, also observed in the Pd analogue,[7] makes the two PMe_3 ligands non equivalent in the NMR time scale at 25 °C, and therefore the $^{31}P\{^1H\}$ NMR spectrum consists of the superposition of two spin systems: the ABX of the ^{196}Pt ($S = {}^1/_2$)-containing molecules (ca. 34%) and the AB that corresponds to other Pt isotopomers. The strong coupling constant between the two phosphorus nuclei ($^2J_{PP}$ = 500 Hz) demonstrates the mutual trans disposition of the phosphine ligands.[15]

Since the reaction of **9** with 1 equiv of PMe_3, already discussed, does not give the monophosphine complex analogue of **1** a different synthetic strategy was devised to prepare the desired mononuclear species Pt[CH-

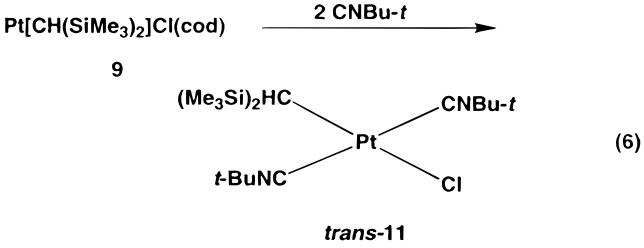
(12) (a) Casey, C. P.; O'Connor, J. M. *Organometallics* **1985**, *4*, 384. (b) Herrmann, W. A.; Kühn, F. E.; Romão, C. C. *J. Organomet. Chem.* **1995**, *489*, C56.

(13) (a) Thomson, S. K.; Young, G. B. *Polyhedron* **1988**, *7*, 1953. (b) Kelly, R. D.; Young, G. B. *Polyhedron* **1989**, *8*, 433.

(14) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

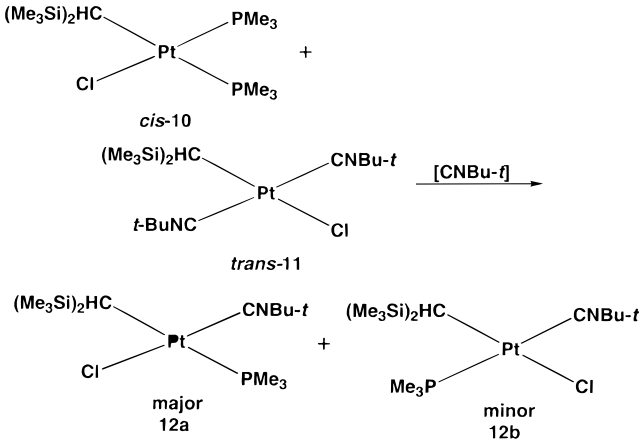
(15) (a) Anderson, G. K.; Black, D. M.; Cross, R. J.; Robertson, F. J.; Rycroft, D. S.; Wat, R. K. M. *Organometallics* **1990**, *9*, 2568. (b) Siedle, A. R.; Gleason, W. B.; Newmark, R. A. *Organometallics* **1986**, *5*, 1969.

$(SiMe_3)_2]Cl(CNBu\text{-}t)(PMe_3)$ (**12**). Treatment of **9** with 2 equiv of CNBu-*t* affords the complex $Pt[CH(SiMe_3)_2]$-$Cl(CNBu\text{-}t)_2$ (**11**) exclusively as the trans isomer (eq 6).



(6)

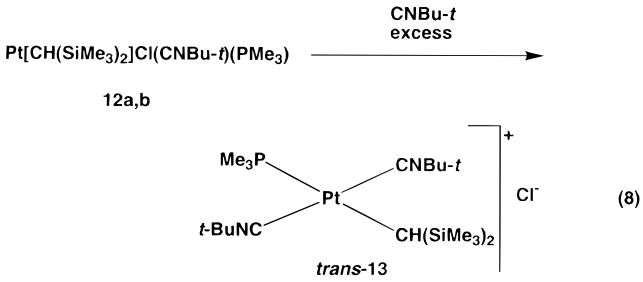
Analytical and spectroscopic data for this complex are collected in the Experimental Section and are in accord with the proposed formulation. When an equimolar mixture of *cis*-**10** and *trans*-**11** is dissolved in Et_2O and treated with a catalytic amount of CNBu-*t* (or PMe_3) a ligand redistribution reaction[16] takes place and complex **12** is generated as a mixture of the two isomers shown in eq 7 (4:1 ratio). The trans configuration of the major



(7)

species, **12a**, is attested by the strong coupling that exists between the methyne carbon, *C*H$(SiMe_3)_2$, and the phosphorus nucleus of the PMe_3 ligand (δ = 16.0, $^2J_{CP}$ = 77 Hz).[13a] As for the minor isomer **12b** the cis disposition of the PMe_3 and chloride ligands can be deduced from the analysis of the ^{195}Pt satellites of ^{31}P-$\{^1H\}$ NMR spectrum (δ −15.3, $^1J_{PPt}$ = 1750 Hz).[14] It is interesting to note that the Pd derivative **2** stereochemistry is identical to the less favored Pt isomer **12b**.

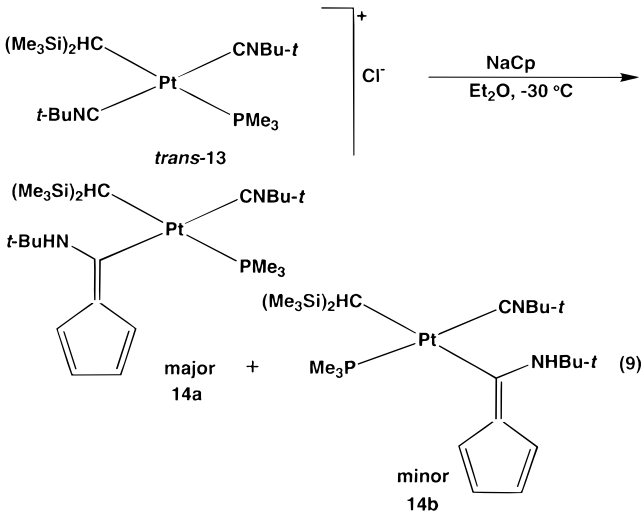
Synthesis and Characterization of Platinafulvene Derivatives. In contrast with the behavior of **2**, the addition of an excess (≥2 equiv) of *tert*-butylisocyanide to **12** results in the isolation (ca. 75% yield) of a pure stable compound. This has been identified as the cationic species $\{Pt[CH(SiMe_3)_2](CNBu\text{-}t)_2(PMe_3)\}Cl$ (**13**) (eq 8). This reaction is not unexpected. In fact, the displacement of a chloride ligand by an isocyanide is a well-known reaction in the chemistry of square-planar Pt(II) complexes.[17] The proposed trans geometry of **13** is based on NMR spectroscopic studies ($^2J_{CP}$ = 54 Hz for the *C*H$(SiMe_3)_2$ carbon nucleus) whereas its ionic formulation is in accord with its low solubility in Et_2O



(8)

and also with the observation of almost identical NMR spectroscopic parameters for the species that results when the chloride anion is replaced by the non coordinating BAr_4^- anion (Ar = 3,5-bis(trifluoromethyl)-phenyl).[18]

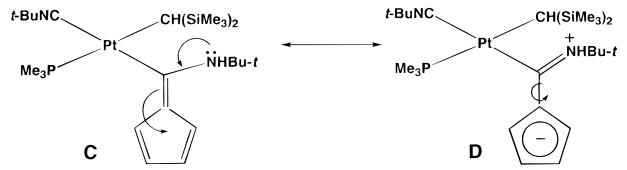
Compound **13** reacts at low temperature with NaCp to produce a mixture of several compounds (^{31}P NMR evidence) (eq 9). One of them, the platinafulvene **14a**



(9)

(δ Pt−*C*H$(SiMe_3)_2$ −3.0, $^2J_{CP}$ = 69 Hz), is isolated as a brown-yellow crystalline solid by crystallization from Et_2O:petroleum ether solutions in ca. 40% yield. The minor isomer **14b** has the PMe_3 cis to both the alkyl and the fulvene ligands (δ −7.5, d, $^2J_{CP}$ = 5 Hz, *C*H-$(SiMe_3)_2$ and δ 195, d, $^2J_{CP}$ = 9 Hz, fulvene *exo* carbon).

As shown in Figure 2, complex **14a** exhibits fluxional behavior in solution. The two rotamers **E** and **F** that are present at low temperatures in a ca. 1:7 ratio (acetone-d_6) interconvert rapidly in the NMR time scale at higher temperatures. They are assigned as **E** and **F** and are proposed to arise from restricted rotation around C−N bond (see canonical form **D**) differing in



the spatial orientation of the Pt and Bu-*t* moieties (**E**, trans; **F**, cis;[19] Figure 2). The major rotamer **F** is

(16) Cooper, D. G.; Powell, J. *J. Am. Chem. Soc.* **1973**, *95*, 1102.
(17) Briggs, J. R.; Constable, A. G.; McDonald, W. S.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1982**, 1225.
(18) Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920.
(19) (a) Cross, R. J.; Davidson, M. F. *J. Chem. Soc., Dalton Trans.* **1988**, 1147. (b) Crociani, B.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1974**, 693.

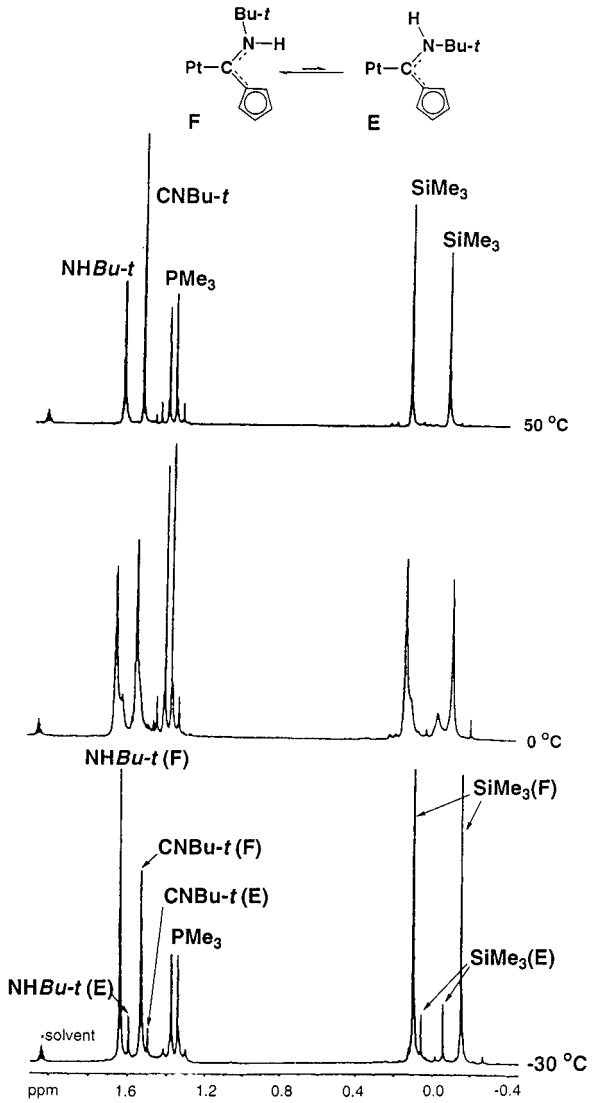


Figure 2. Variable temperature ^{1}H NMR spectra of **14a** (acetone-d_6) in the range from 2.0 to −0.4 ppm.

characterized by a $^3J_{HPt}$ coupling of 105 Hz between the N−H proton and the ^{195}Pt nucleus whereas for the minor, **E**, a value of ca. 40 Hz can be extracted from the ^{1}H NMR spectrum recorded in toluene at −30 °C. These data are similar to those previously reported for related species.[19b] In keeping with these considerations only two resonances due to the C_5H_4 fragment can be observed in the ^{1}H NMR spectrum in the fast-exchange regime.

Interestingly the minor isomer **14b**, which has trans PMe_3 and CNBu-*t* ligands (see eq 9), does not exhibit any sign of fluxionality and resembles in this regard the palladafulvene compounds already described. Hence for this species canonical form **D** has a smaller contribution to the electronic structure thereby explaining the higher double-bond character of the C_{exo}−C_5H_4 linkage and the faster rotation around the C_{exo}−N bond. The $^3J_{HPt}$ value of 70 Hz found for the amine proton of this complex clearly indicates the presence of fast equilibrating rotamers of types **E** and **F**.

Discussion

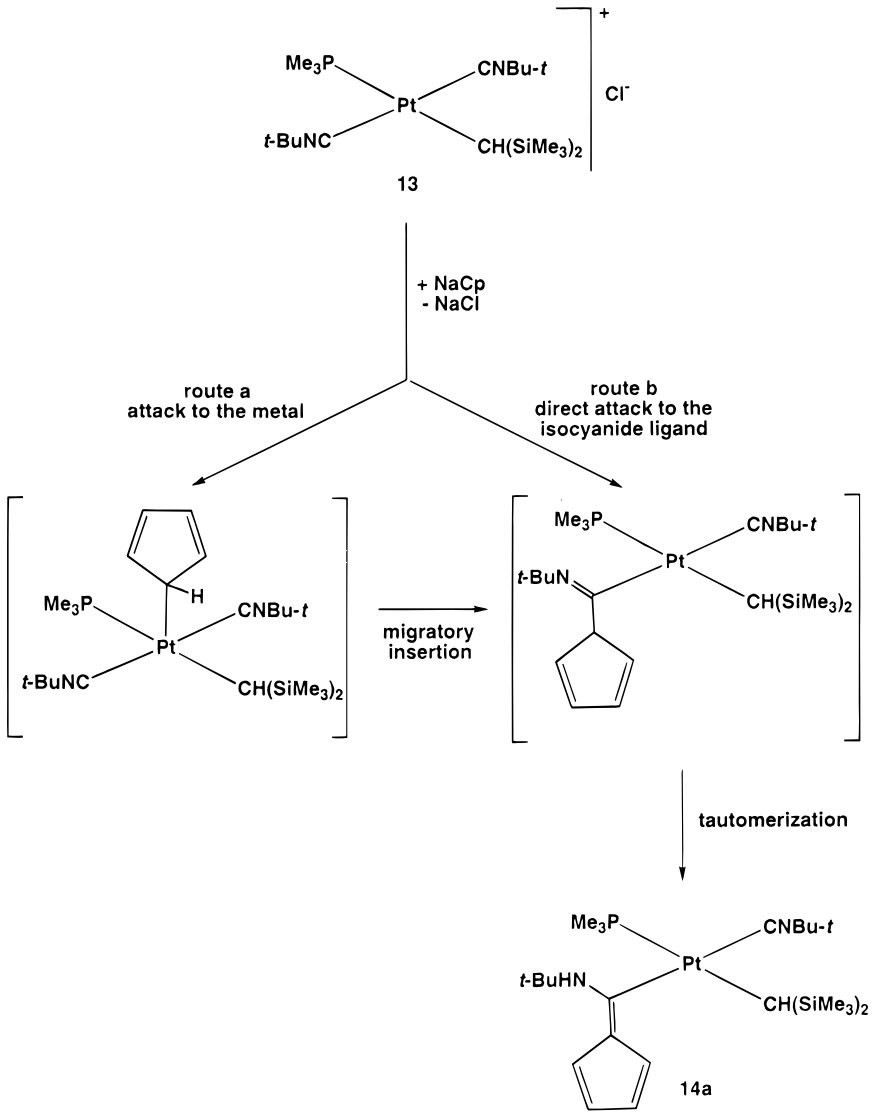
It appears reasonable to suggest that iminoacyl complexes of type **A**, formally derived from the migratory insertion of CNBu-*t* into a M−η^1-Cp′ or M−η^1-Ind linkage, are initially formed in the reactions leading to the metallafulvene complexes described in this paper. Subsequent tautomerization to the more stable enamine form (see for example **B**) leads to final products of these reactions. A similar transformation has been advanced to explain the generation of the keteneimine Ph_3HC_4=C=CNR in the reaction of $PdCl_2(CNR)_2$ with KC_5Ph_3H, but the purported palladafulvene complex intermediate could not be detected.[20] To our knowledge compounds **4**, **5**, **6**, and **14** find no precedent in the literature, even though complexes of the transition metals that contain fulvene ligands are well-known.[21] In our view, their closest analogues are some cobaltafulvenes that possess a Co=C−CH=CH−CH=CH delocalized fragment[22] and a recently described tungsten derivative that has an N-deprotonated 6-aminofulvene ligand.[10]

The higher stability of the enamine form **B**, as compared to the iminoacyl structure **A**, is unusual in transition metal chemistry, where the imine formulation is clearly predominant.[23] Moreover, organic enamines that contain a hydrogen atom bonded to nitrogen are commonly unstable with respect to their imine tautomers.[24] It is evident that the adoption of the enamine structure in the compounds described herein is due to the stability of the fulvene moiety, doubtless associated with the extensive electronic delocalization of this structure.[25]

In closing, some comments devoted to the mechanism of the reaction that leads to the proposed iminoacyl products with structure of type **A** appear appropriate. Two reactions pathways, routes **a** and **b** of Scheme 3, may be considered. The first involves initial attack at the metal cationic center by Cp′ or indenyl ligand followed by a migratory insertion reaction. The second implicates direct attack at a coordinated isocyanide ligand. Despite our efforts we have been unable to distinguish conclusively between these possibilities. The observation of more than one stereoisomer in some of these reactions (for example **14a** and **14b**, eq 9) would be in favor of route **a** since a neutral five-coordinate species of the kind illustrated in Scheme 3 could readily undergo isomerization even at low temperatures. There is precedent in the literature for Pd− and Pt−η^1-Cp complexes[26] as well as for five-coordinated M(II) compounds of these elements.[27] Furthermore, as already

(20) Tanese, T.; Fukushima, T.; Nomura, T.; Yamamoto, Y. *Inorg. Chem.* **1994**, *33*, 32.
(21) (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. (h) Teuber, R.; Köppe; Linti, G.; Tacke, M. *J. Organomet. Chem.* **1997**, *545*−*546*, 105.
(22) Wadepohl, H. *Comments Inorg. Chem.* **1994**, *15*, 369.
(23) For some exceptions, see: Cámpora, J.; Hudson, S. A.; Carmona, E. *Organometallics* **1995**, *14*, 2151 and references therein.
(24) (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.
(25) Bergman, E. D. *Chem. Rev.* **1968**, *68*, 41.
(26) Anderson, G. K. *Synlett* **1995**, 681.
(27) Canty, A. J.; van Koten, G. *Acc. Chem. Res.* **1995**, *28*, 406.

Scheme 3



mentioned related reactions that involve formal migratory insertions of unsaturated molecules into M−η^1-Cp bonds are known.[4a] Notwithstanding the above, the observations summarized in Scheme 3 are also consistent with route **b**, i.e., with a direct attack onto the coordinated isocyanide ligand.

As already mentioned, the addition of 2 equiv of CNBu-*t* to a solution of the palladium-indenyl complex **7** in THF-d_8, maintained at −50 °C, gives the η^1-indenyl derivative **8**. Subsequent reaction with 1 equiv of NaCp at −30 °C leads to the fulvene complexes **4** and **6** in ca. 1:1 ratio, along with very small amounts of the η^5-C_5H_5 derivative **3** (Scheme 4). These results may be interpreted by assuming indenyl displacement by the isocyanide[28] and formation of an undetected cationic bis(isocyanide) complex of palladium analogous to **13** that contains an η^0-Cp or η^0-Ind group as the counteranion,[3,29] that is, with the generation of the fulvene derivatives entailing a direct attack onto a coordinated isocyanide ligand. Similar mechanistic proposals have been suggested for somewhat related processes.[30] Hence, as already indicated, it is not clear whether our fulvene compounds are formed by either route **a** or **b**, the additional possibility also exists that both pathways may be operative under the reaction conditions.

Experimental Section

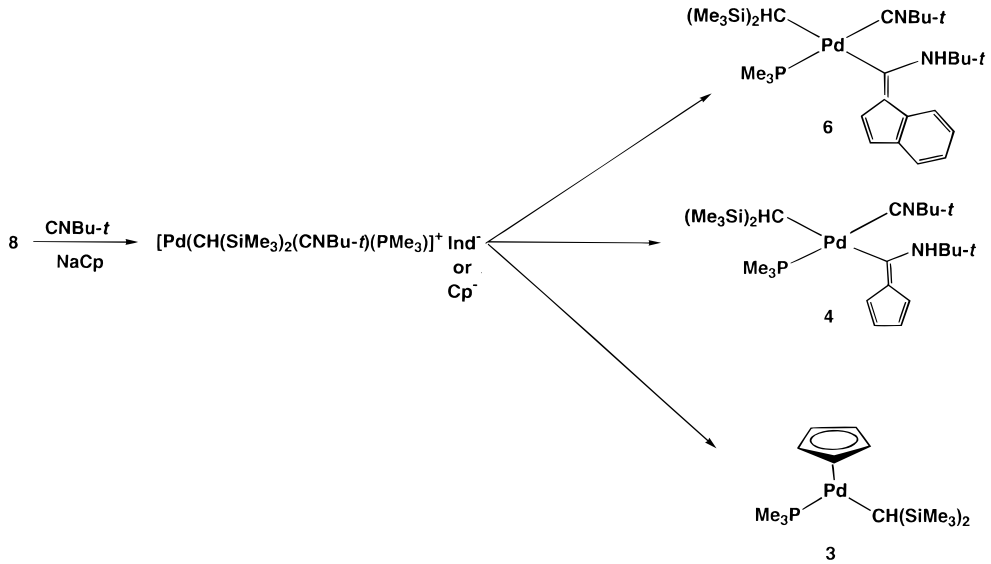
Microanalyses were performed by the Analytical Service of the University of Seville. The spectroscopic instruments used were Perkin-Elmer models 577 and 684 for IR spectra and Bruker AMX-300 and AMX-500 for NMR spectroscopy. Spectra are referenced to external $SiMe_4$ using the residual protio solvent peaks as internal standards (^{1}H NMR experiments) or the characteristic resonances of the solvent nuclei (^{13}C NMR experiments). ^{31}P{^{1}H} NMR chemical shifts are referenced to external 85% H_3PO_4. All preparations and other operations were carried out under oxygen-free nitrogen by conventional Schlenk techniques. Solvents were dried and degassed before use. The petroleum ether used had a boiling point of 40−60 °C. NaCp was prepared from NaH and freshly cracked

(28) For a related process, see: Butts, M. D.; Bergman, R. G. *Organometallics* **1994**, *13*, 1899.

(29) (a) Marder, T. B.; Williams, I. D. *J. Chem. Soc., Chem. Commun.* **1987**, 1478. (b) Kakkar, A. K.; Taylor, N. J.; Marder, T. B. *Organometallics* **1989**, *8*, 1765.

(30) For an example of a nucleophilic attack of a free indenyl anion to one of the double bonds of a coordinated COD in a Ir(I) complex, see: Merola, J. S.; Kacmarck, R. T. *Organometallics* **1989**, *8*, 778.

Scheme 4



dicyclopentadiene. Compounds $\{Pd[CH(SiMe_3)_2](\mu\text{-}Cl)(PMe_3)\}_2$ (**1**), (η^3-Ind)$Pd[CH(SiMe_3)_2](PMe_3)$ (**7**)[7] and $PtCl_2(cod)$[31] were prepared according to the reported procedures.

Preparation of Pd[CH(SiMe$_3$)$_2$]Cl(CNBu-*t*)(PMe$_3$) (2). CNBu-*t* (0.36 mmol, 0.36 mL of a 1 M solution in THF) was added to a cold (−30 °C) solution of complex **1** (0.14 g, 0.18 mmol) in Et_2O (10 mL). An instantaneous discoloration was observed and the mixture stirred at that temperature for 30 min. The solvent was stripped off in vacuo, and the white residue was extracted with a mixture of petroleum ether and Et_2O (1:1). Concentration and cooling at −30 °C provided compound **2** as a white crystalline solid in essentially quantitative yield. IR (Nujol): ν(CN) 2200 cm^{-1}. ^{1}H NMR (C_6D_6, 25 °C) δ 0.18 (d, $^3J_{HP}$ = 12.0 Hz, 1H, C*H*(SiMe$_3$)$_2$), 0.28 (s, 18H, SiMe$_3$), 0.93 (s, 9H, CNCMe$_3$), 1.12 (d, $^2J_{HP}$ = 10.2 Hz, 9H, PMe$_3$); ^{13}C{^{1}H} NMR (C_6D_6, 25 °C) δ 4.0 (SiMe$_3$), 7.8 (*C*H-(SiMe$_3$)$_2$), 13.8 (d, $^1J_{CP}$ = 32 Hz, PMe$_3$), 29.0 (C*Me*$_3$), 56.7 (*C*Me$_3$), 138.2 (d, $^2J_{CP}$ = 170 Hz, *C*NBu-*t*); ^{31}P{^{1}H} NMR (C_6D_6, 25 °C) δ −8.1.

Preparation of Pd[C(NHBu-*t*)=C(C$_4$H$_4$)][[CH(SiMe$_3$)$_2$]-(CNBu-*t*)(PMe$_3$) (4). A solution of complex **1** (0.19 g, 0.25 mmol) in Et_2O (30 mL) was cooled to −30 °C and treated with a solution of CNBu-*t* in THF (2.6 mL, 0.57 M, 1.48 mmol). The solution became colorless, and the formation of a white precipitate was observed. After stirring for 30 min at this temperature, a solution of NaCp was added (1.3 mL, 0.37 M, 0.48 mmol). The orange mixture formed was maintained at −30 °C for 15 min and after stirring for the same period of time at room temperature the solvent was evaporated under vacuo, and the residue was extracted with a mixture of petroleum ether/ethyl ether (30 mL, 2:1) and filtered. After concentration and cooling at −30 °C, complex **4** was obtained as white crystals (0.13 g, 45%). Anal. Calcd for $C_{25}H_{43}N_2Si_2PPd$: C, 52.38; H, 8.97; N, 4.89. Found: C, 51.95; H, 8.85; N, 4.60. IR (Nujol): ν(NH) 3322, ν(CN) 2190 and 1508 cm^{-1}. ^{1}H NMR (C_6D_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, CNC*Me*$_3$), 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_2Cl_2, 25 °C) δ 0.5 (d, $^2J_{CP}$ = 5 Hz, *C*H(SiMe$_3$)$_2$), 4.6 (SiMe$_3$), 5.0 (SiMe$_3$),15.1 (d, $^1J_{CP}$ = 32 Hz, PMe$_3$), 29.6 (C*Me*$_3$), 31.4 (NHC*Me*$_3$), 53.5 (*C*Me$_3$), 57.7 (NH*C*Me$_3$), 102.2, 114.7, 120.4, 123.6 (CH$_{fulv}$), 129.2 (C=*C*C$_4$H$_4$), 139.1 (d, $^2J_{CP}$ = 154 Hz, *C*NBu-*t*), 206.0 (d, $^2J_{CP}$ = 9 Hz, C=*C*C$_4$H$_4$). ^{31}P{^{1}H} NMR (C_6D_6, 25 °C) δ −15.0.

(31) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521.

Preparation of Pd[C(NHBu-*t*)=C(C$_4$H$_3$Me)][CH(SiMe$_3$)$_2$]-(CNBu-*t*)(PMe$_3$) (5). The methylcyclopentadienyl derivative **5** was obtained as a mixture of stereoisomers (NMR evidence) following a similar procedure to that described above but using NaC_5H_4Me. Fractional crystallization at −30 °C from petroleum ether solutions afforded only one stereoisomer, **5a**, as white crystals. Yield 40%. IR (Nujol): ν(NH) 3330, ν(CN) 2182 and 1520 cm^{-1}. ^{1}H 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, $^4J_{HMe}$ = 1.1 Hz, 1H, CH$_{fulv}$), 6.66 (dd, $^3J_{HH}$ = 4.4 Hz, $^3J_{HH}$ = 2.6 Hz, 1H, CH$_{fulv}$), 6.99 (br s, 1H, NH), 7.16 (dd, $^3J_{HH}$ = 4.4 Hz, $^4J_{HH}$ = 2.2 Hz, 1H, CH$_{fulv}$); ^{13}C{^{1}H} NMR (C_6D_6, 25 °C) δ −0.3 (d, $^2J_{CP}$ = 6 Hz, *C*H(SiMe$_3$)$_2$), 4.9 (SiMe$_3$), 5.3 (SiMe$_3$), 14.5 (d, $^1J_{CP}$ = 31 Hz, PMe$_3$), 19.0 (*Me*-CC$_4$H$_3$), 28.9 (C*Me*$_3$), 31.4 (NHC*Me*$_3$), 57.5 (*C*Me$_3$), 57.7 (NH-*C*Me$_3$), 115.0, 120.0, 124.6 (CH$_{fulv}$), 117.1 (C=C*C*(Me)C$_3$H$_3$), 129.0 (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=*C*C(Me)C$_3$H$_3$); ^{31}P{^{1}H} NMR (C_6D_6, 25 °C) δ −16.3.

Preparation of Pd[C(NHBu-*t*)=C(C$_8$H$_6$)][[CH(SiMe$_3$)$_2$]-(CNBu-*t*)(PMe$_3$) (6). A solution of the dimer **1** (0.22 g, 0.28 mmol) in Et_2O (25 mL) was treated, at −30 °C, with a solution of CNBu-*t* in THF (1.2 mL, 1 M, 1.2 mmol). The solution became colorless, and, after stirring for 30 min at low temperature, a solution of LiInd (0.57 mmol, prepared by reaction of a solution of indene in Et_2O with *n*-BuLi) was added. The intense yellow mixture was stirred at −30 °C for 30 min and then taken to dryness. The resulting oily residue was redissolved in Et_2O (3 mL), and purification was achieved by chromatography at −15 °C (alumina as the static phase and a 1:1 mixture of light petroleum/Et_2O as eluant). Compound **6** was recovered as a yellow band and concentration of this fraction, and cooling to −30 °C provided the product as a yellow powder. Yield 0.14 g (40%). Anal. Calcd for $C_{29}H_{53}N_2Si_2PPd$: C, 55.89. Found: C, 55.59; H, 8.56; N, 4.57.; H, 8.51; N, 4.49. IR (Nujol): ν(NH) 3390, ν(CN) 2180 and 1530 cm^{-1}. ^{1}H NMR (C_6D_6, 25 °C) δ −0.66 (d, $^3J_{HP}$ = 14.0 Hz, 1H, C*H*(SiMe$_3$)$_2$), 0.37 (s, 9.0 H, SiMe$_3$), 0.51 (s, 9H, SiMe$_3$), 0.76 (s, 9H, CNCMe$_3$), 0.87 (d, $^2J_{HP}$ = 9 Hz, 9H, PMe$_3$), 1.40 (s, 9H, NHC*Me*$_3$), 6.99 (d, $^3J_{HH}$ = 4.7 Hz, 1H, CH$_{cpring}$), 7.27 (br s, 1H, NH), 7.29 (t, $^3J_{HH}$ = 7.5 Hz, 1H, CH$_{benzring}$), 7.38 (t, $^3J_{HH}$ = 7.5 Hz, 1H, CH$_{benzring}$), 7.76 (d, $^3J_{HH}$ = 4.7 Hz, 1H, CH$_{cpring}$), 7.83 (d, $^3J_{HH}$ = 7.4 Hz, 1H, CH$_{benzring}$), 7.94 (d, $^3J_{HH}$ = 7.7 Hz, 1H, CH$_{benzring}$); ^{13}C{^{1}H} NMR (C_6D_6, 25 °C) δ −0.1 (d, $^2J_{CP}$ = 5 Hz, *C*H(SiMe$_3$)$_2$), 4.9 (SiMe$_3$), 5.2 (SiMe$_3$), 14.5 (d, $^1J_{CP}$ = 30 Hz,

PMe_3), 28.7 (CMe_3), 31.4 ($NHCMe_3$), 52.8 (CMe_3), 56.9 ($NHCMe_3$), 112.4, 118.0 (CH_{cpring}), 119.8 ($C{=}CC_8H_6$), 120.3, 120.8, 134.3 ($CH_{benzring}$), 129.9. 140.6 (C_q), 196.7 (d, $^2J_{CP}$ = 9 Hz, $C{=}CC_8H_6$); $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C) δ −16.1.

Reaction of Complex 7 with CNBu-*t*. Formation of Pd(η^1-C_9H_7)[CH($SiMe_3$)$_2$](CNBu-*t*)(PMe_3) (8). A solution of complex **5** (13 mg, 0.03 mmol) in 0.5 mL of CD_2Cl_2 was placed in an NMR tube and treated at −70 °C with approximately 2 equiv of CNBu-*t* (7.5 μL). ^1H and $^{31}P\{^1H\}$ NMR spectra, registered at −50 °C, showed the quantitative formation of compound **8**. When warmed to room-temperature decomposition of **8** was observed giving the metallafulvene **6** (30%, NMR) plus other unidentified species. Data for **8**: ^1H NMR (CD_2Cl_2, −50 °C) δ −0.48 (d, $^3J_{HP}$ = 19.6 Hz, 1H, C*H*($SiMe_3$)$_2$), 0.13 (s, 9H, $SiMe_3$), 0.22 (s, 9H, $SiMe_3$), 1.01 (s, 9H, $CNCMe_3$), 1.27 (d, $^2J_{HP}$ = 8.9 Hz, 9H, PMe_3), 5.37 (br s, 1H, CH_{cpring}), 6.55 (t, 1H, $^3J_{HH}$ = 3.8 Hz, CH_{cpring}), 6.93 (m, 2H, $CH_{benzring}$), 7.02 (m, 1H, CH_{cpring}), 7.43 (d, $^3J_{HH}$ = 6.9 Hz, 1H, $CH_{benzring}$), 7.51 (d, $^3J_{HH}$ = 7.0 Hz, 1H, $CH_{benzring}$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −50 °C): δ 3.9 ($SiMe_3$), 4.6 ($SiMe_3$), 16.9 (d, $^1J_{CP}$ = 29 Hz, PMe_3), 29.6 (coordinated $CNCMe_3$), 30.3 (free $CNCMe_3$), 48.2 (d, $^2J_{CP}$ = 69 Hz, Pd−*C*H(ind)), 56.5 ($CNCMe_3$), 115.6 (d, $^3J_{CP}$ = 6 Hz, CH_{cpring}), 120.1, 120.7, 120.8, 122.6 ($CH_{benzring}$), 139.7 (CH_{cpring}), 141.4 (C_q), 153.5 (d, $^2J_{CP}$ = 4 Hz, coordinated *C*NBu-*t*); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −50 °C) δ −16.6.

Reaction of Complex 7 with 2 Equiv of CNBu-*t* and 1 Equiv of NaCp. To a solution of complex **7** in CD_2Cl_2 (0.5 mL), at −30 °C, was added CNBu-*t* (10.5 μL). After 10 min at this temperature, 1 equiv of NaCp (0.1 mL, 0.19 M in THF) was added by syringe into this solution. The resulting mixture was inmediately studied by NMR spectroscopy, and after 30 min the ^1H NMR spectrum showed two doublets at δ −0.69 ($^3J_{HP}$ = 14.5 Hz) and −0.71 ($^3J_{HP}$ = 14.5 Hz) that correspond to the two possible fulvene species **4** and **6**, together with a less intense doublet at δ −1.21 ($^3J_{HP}$ = 11.2 Hz) due to the presence of **3**. The $^{31}P\{^1H\}$ NMR spectrum consisted of two singlets at δ −15.2 and −15.6 assigned to the two fulvene complexes, and one singlet at δ −4.4 for **3** (5:5:1 ratio, respectively). When 4 equiv of CNBu-*t* was used in the reaction, the mentioned ratio of these species was 15:15:1.

Preparation of Pt[CH($SiMe_3$)$_2$]Cl(cod) (9). To a cold (−70 °C) stirred suspension of $PtCl_2$(cod) (2.35 g, 6.28 mmol) in Et_2O (30 mL) was added a solution of Mg[CH($SiMe_3$)$_2$]Cl in Et_2O (28 mL, 0.22 N, 6.28 mmol) dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 3 days. Filtration, concentration, and cooling to −30 °C furnished complex **9** as white crystals. Yield 1.6 g (45%). Anal. Calcd for $C_{15}H_{31}Si_2ClPt$: C, 36.16; H, 6.23. Found: C, 36.23; H, 6.44. ^1H NMR ($CDCl_3$, −60 °C) δ 0.12 (s, 18H, $SiMe_3$), 0.57 (s, $^2J_{HPt}$ = 64 Hz, 1H, C*H*($SiMe_3$)$_2$), 2.1−2.6 (m, 8H, CH_2(cod)), 4.42 (m, $^2J_{HPt}$ = 73 Hz, 2H, CH(cod)), 5.35 (m, $^2J_{HPt}$ = 36 Hz, 2H, CH(cod)); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C) δ 4.2 ($SiMe_3$), 23.2 ($^1J_{CPt}$ = 570 Hz, *C*H($SiMe_3$)$_2$), 28.2 ($^2J_{CPt}$ = 9 Hz, CH_2(cod)), 31.7 ($^2J_{CPt}$ = 10 Hz, CH_2(cod)), 85.0 ($^1J_{CPt}$ = 213 Hz, CH(cod)), 111.3 ($^2J_{CPt}$ = 42 Hz, CH(cod)).

Preparation of Pt[CH($SiMe_3$)$_2$]Cl(PMe_3)$_2$ (10). PMe_3 (1.2 mmol, 1.2 mL of a 1 M solution in THF) was added to a solution of complex **9** (0.26 g, 0.52 mmol) in Et_2O (15 mL) at room temperature. After stirring for 8 h, the reaction mixture was taken to dryness and the resulting oily white residue was extracted into a 2:1 mixture of petroleum ether/Et_2O. Crystallization at −30 °C afforded only the cis isomer as white crystals (0.14 g, 50%). Concentration of the mother liquor and cooling at −30 °C provided white crystals of the trans isomer (0.03 g, 10%). Anal. Calcd for $C_{13}H_{37}Si_2P_2ClPt$: C, 28.79; H, 6.83. Found: C, 28.43; H, 7.01. Data for *cis*-**10**: ^1H NMR (C_6D_6, 25 °C) δ 0.05 (s, 18H, $SiMe_3$), 0.18 (dd, $^3J_{HP}$ = 11.0, $^3J_{HP}$ = 9.0 Hz, 1H, C*H*($SiMe_3$)$_2$), 1.02 (d, $^2J_{HP}$ = 10.0 Hz, 9H, PMe_3), 1.06 (d, $^2J_{HP}$ = 8.9 Hz, 9H, PMe_3); $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C) δ 6.1 ($SiMe_3$), 11.8 (d, $^2J_{CP}$ = 77 Hz, $^1J_{CPt}$ = 477 Hz, *C*H($SiMe_3$)$_2$), 14.8 (d, $^1J_{CP}$ = 30 Hz, PMe_3), 17.3 (dd, $^1J_{CP}$ = 42 Hz, $^2J_{CP}$ = 3 Hz, PMe_3); $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C) δ −17.3 (d, $^2J_{PP}$ =15, $^1J_{PPt}$ = 1830 Hz) and −28.2 (d, $^2J_{PP}$ = 15, $^1J_{PPt}$ = 4150 Hz). Data for *trans*-**10**: ^1H NMR (C_6D_6, 25 °C) δ 0.03 (s, 9H, $SiMe_3$), 0.06 (s, 9H, $SiMe_3$), 0.48 (dd, $^3J_{HP}$ = 15.0 Hz, $^3J_{HP}$ = 10.0 Hz, 1H, C*H*($SiMe_3$)$_2$), 1.46 (dd, $^2J_{HP}$ = 8.6 Hz, $^3J_{HP}$ = 1.0 Hz, 9H, PMe_3), 1.56 (dd, $^2J_{HP}$ = 8.4 Hz, $^3J_{HP}$ = 2.0 Hz, 9H, PMe_3); $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C) δ −12.0 (d, $^2J_{PP}$ = 500 Hz, $^1J_{PPt}$ = 2760 Hz) and −19.1 (d, $^2J_{PP}$ = 500 Hz, $^1J_{PPt}$ = 2840 Hz).

Preparation of Pt[CH($SiMe_3$)$_2$]Cl(CNBu-*t*)$_2$ (11). To a solution of compound **9** (0.26 g, 0.52 mmol) in Et_2O (15 mL) was added a solution of CNBu-*t* in toluene (2.2 mL, 0.49 M, 1.04 mmol) at room temperature, and the mixture stirred for a period of 8 h. The solvent was removed completely in vacuo, and the resulting oily residue crystallized from petroleum ether at −30 °C to give **11** as a white microcrystalline solid. Yield 0.14 g (50%). Anal. Calcd for $C_{17}H_{37}N_2Si_2ClPt$: C, 36.71; H, 6.66; N, 5.04. IR (Nujol): ν(CN) 2192 cm^{-1}. Found: C, 36.93; H, 6.75; N, 4.69. ^1H NMR ($CDCl_3$, 25 °C) δ 0.05 (s, 18H, $SiMe_3$), 0.42 (s, $^2J_{HPt}$ = 93 Hz, 1H, C*H*($SiMe_3$)$_2$), 1.52 (s, 18H, $CNCMe_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C) δ −7.5 ($^1J_{CPt}$ = 509 Hz, *C*H($SiMe_3$)$_2$), 3.71 ($SiMe_3$), 29.9 (CMe_3), 58.0 (CMe_3), 129.5 ($CNCMe_3$).

Preparation of Pt[CH($SiMe_3$)$_2$]Cl(CNBu-*t*)(PMe_3) (12). To a mixture of complexes *cis*-**10** (0.045 g, 0.08 mmol) and **11** (0.045 g, 0.08 mmol) in Et_2O (10 mL) was added a trace of CNBu-*t*, and the mixture stirred for 8 h at room temperature. After that period, the solvent was evaporated under reduced pressure and the product extracted into 10 mL of a mixture of petroleum ether/Et_2O (3:1). By concentration and cooling to −30 °C, a white crystalline solid was obtained. Yield 0.048 g (50%). Anal. Calcd for $C_{15}H_{37}NSi_2PClPt$: C, 32.8; H, 6.74; N, 2.55. Found: C, 33.10; H, 6.95; N, 2.52. IR (Nujol): ν(CN) 2178 cm^{-1}. Data for the major species **12a**: ^1H NMR ($CDCl_3$, 25 °C) δ 0.45 (s, 18H, $SiMe_3$), 0.97 (s, 9H, $CNCMe_3$), 1.09 (d, $^2J_{HP}$ = 10.0 Hz, 9H, PMe_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C) δ 4.4 ($SiMe_3$), 14.1 (d, $^1J_{CP}$ = 30 Hz, PMe_3), 16.0 (d, $^2J_{CP}$ = 77 Hz, *C*H($SiMe_3$)$_2$), 30.0 (CMe_3), 58.0 (CMe_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C) δ −18.0 ($^1J_{PPt}$ = 1660 Hz). Data for the minor species **12b**: ^1H NMR ($CDCl_3$, 25 °C) δ 0.64 (s, 18H, $SiMe_3$), 0.87 (s, 9H, $CNCMe_3$), 1.06 (d, $^2J_{HP}$ = 10.0 Hz, 9H, PMe_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ −15.3 ($^1J_{PPt}$ = 1750 Hz).

Preparation of {Pt[CH($SiMe_3$)$_2$](CNBu-*t*)$_2$(PMe_3)}Cl (13). To a solution of complex **12** (0.13 g, 0.24 mmol) in Et_2O (10 mL) was added a solution of CNBu-*t* in THF (0.74 mL, 1 M, 0.74 mmol) at room temperature. After approximately 5 min, the precipitation of a white solid was observed and the reaction mixture stirred for 30 min. The solvent was completely evaporated leaving a white solid. This residue was washed with petroleum ether (10 mL) and dried in vacuo. Yield 0.11 g (75%). A sample of this complex of microanalytical purity has proved difficult to be obtained. The formation of this complex is however secured by the isolation of the related BAr_4^- derivative (see below) which gives reliable analytical data. ^1H NMR ($CDCl_3$, 25 °C) δ 0.15 (s, 18H, $SiMe_3$), 0.70 (d, $^3J_{HP}$ = 8.0, $^2J_{HPt}$ = 71 Hz, 1H, C*H*($SiMe_3$)$_2$), 1.95 (d, $^2J_{HP}$ = 10.0 Hz, 9H, PMe_3) 1.63 (s, 18H, $CNCMe_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C) δ 4.3 ($SiMe_3$), 7.6 (s, $^2J_{CP}$ = 54 Hz, $^1J_{CPt}$ = 332 Hz, *C*H($SiMe_3$)$_2$), 15.6 (d, $^1J_{CP}$ = 35 Hz, PMe_3), 29.8 and 29.9 (CMe_3), 60.3 and 60.6 (CMe_3), 125.8 ($^1J_{CPt}$ = 1460 Hz, $CNCMe_3$), and 127.3 ($^1J_{CPt}$ = 1430 Hz, $CNCMe_3$); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C) δ −21.5 ($^1J_{PPt}$ = 1560 Hz).

Preparation of Complex 13 with BAr_4^- as the Counterion (Ar = 3,5-Bis(trifluoromethyl)phenyl). Complex **13** (0.10 g, 0.18 mmol) and $NaBAr_4$ (0.16 g, 0.18 mmol) were dissolved in Et_2O (15 mL) at room temperature. The formation of a cloudy precipitate was immediately observed. After 15 min of stirring the reaction mixture was filtered, the volume of the resulting solution was reduced to 5 mL and then cooled to −70 °C. Petroleum ether (10 mL) was then added, and the pale yellow solid obtained isolated by filtration and dried under vacuum. Yield: 0.14 g (50%). IR (Nujol): ν(CN) 2200 cm^{-1}.

Anal. Calcd for $C_{52}H_{58}F_{24}N_2BSi_2PPt$: C, 42.77; H, 3.97; N, 1.91. Found: C, 42.05; H, 3.92; N, 1.84.

Preparation of Pt[C(NHBu-*t*)=C(C_4H_4)][CH($SiMe_3$)$_2$]-(CNBu-*t*)(PMe_3) (14). To a cold (−30 °C) suspension of complex **13** (0.08 g, 0.128 mmol) in Et_2O (20 mL) was added a solution of NaCp in THF (3.2 mL, 0.04 M, 0.13 mmol) via syringe. The cooling bath was removed, and as it was warmed, the reaction mixture developed a yellow coloration. After 30 min at room temperature, the solvent was removed in vacuo, leaving a brown residue. ^{1}H and ^{31}P{^{1}H} NMR spectroscopy showed that the residue was comprised of a mixture of **14a** and **14b**, in an approximate 2:1 molar ratio, and, of a third unidentified species. After extraction into a 2:1 mixture of light petroleum/Et_2O (15 mL) the solution was filtered. The resulting yellow solution was reduced in volume and cooled to −30 °C to afford the major isomer **14a** as brown-yellow crystals (0.035 g, 40%). Anal. Calcd for $C_{25}H_{53}N_2Si_2PPt$: C, 45.36; H, 7.77; N, 4.23. Found: C, 45.45; H, 7.80; N, 3.90. IR (Nujol): ν(NH) 3350, ν(CN) 2160 and 1520 cm^{-1}. Data for the major species **14a**: ^{1}H NMR (CD_3COCD_3, −50 °C) δ −0.18 (s, 9H, $SiMe_3$), 0.08 (s, 9H, $SiMe_3$), 1.35 (d, $^2J_{HP}$ = 10.0 Hz, 9H, PMe_3), 1.48 (s, 9H, CNCMe_3), 1.58 (s, 9H, NHCMe_3), 5.70 (m, 1H, CH_{fulv}), 5.74 (m, 1H, CH_{fulv}), 6.14 (m, 1H, CH_{fulv}), 6.60 (m, 1H, CH_{fulv}), 7.60 (br s, $^3J_{HPt}$ = 105 Hz, 1H, NH); ^{13}C{^{1}H} NMR (CD_3COCD_3, −50 °C) δ −3.0 (d, $^2J_{CP}$ = 69 Hz, *C*H($SiMe_3$)$_2$), 5.6 ($SiMe_3$), 6.5 ($SiMe_3$),13.9 (d, $^1J_{CP}$ = 33 Hz, PMe_3), 29.9 (CNCMe_3), 31.4 (NHCMe_3), 54.3 (CN*C*Me_3), 59.1 (NH*C*Me_3), 105.1, 113.9, 115.6, 124.8 (CH_{fulv}), 128.4 (C=*C*C_4H_4), 193.8 (d, $^2J_{CP}$ = 11 Hz, C=*C*C_4H_4); ^{31}P{^{1}H} NMR (CD_3COCD_3, −50 °C): δ −24.2 (s, $^1J_{PPt}$ = 1970 Hz).

X-ray Structure Determination of Complex 5a. The crystal selected for the X-ray study contained half a molecule of 1,2-dimethoxyethane of crystallization per asymmetric unit. Crystallographic data can be found in Table 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 AFC6S-Rigaku single-crystal diffractometer. The cell parameters were obtained from the settings of 25 reflections ranged 11.61 < θ < 17.73°. The data were collected in the interval 5 < θ < 45°, using the ω−2θ scan method at a speed of 8°/min. The standard reflections were intensity controlled for decay correction (the final decay was 16%). Absorption (ψ scan method and transmission factors ranged 0.93−1.00), 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 the 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,[32] running on a DEC VAX 3520 at the Servicios Centralizados de Ciencia y Tecnología, Universidad de Cádiz.

Table 2. Crystal and Refinement Data for 5a

empirical formula	$PdC_{29}H_{53}PN_2Si_2 \cdot {}^1/_2C_4H_{10}O_2$
fw	632.32
cryst syst	triclinic
space group	*P*1
a (Å)	16.254(5)
b (Å)	11.101(2)
c (Å)	11.081(2)
α (deg)	90.60(2)
β (deg)	70.52(2)
γ (deg)	83.78(2)
U (Å^3)	1872(2)
Z	2
F(000)	674
D_c (g cm^{-3})	1.122
temp (K)	290
cryst dimens (mm)	0.28 × 0.15 × 0.36
diffractometer	AFC6S-Rigaku
radiation	graphite-monochromated Mo Kα (λ = 0.710 69 Å)
μ(Mo Kα) (cm^{-1})	6.12
scan technique	ω/2θ
scan rate	8.0°/min (in ω) (3 scans)
scan width	(1.05 + 0.30 tan)°
θ_{max}	45.1°
no. of reflcns measd	total: 5104 unique: 4898 (R_{int} = 0.080)
detector aperture	6.0 mm horizontal 6.0 mm vertical
no. of obsd data ($I \geq 3(I)$)	2654
structure solution	Patterson method
refinement	full-matrix least-squares
function minimized	$w(\|F_o\| - \|F_c\|)^2$
least-squares weights	$4F_o^2/^2(F_o^2)$
p-factor	0.03
anomalous dispersion	all non-hydrogen atoms
reflcn/param ratio	8.83
R_F (%)	5.1
R_w (%)	5.5
goodness of fit indicator	1.24
max shift/error	0.03
abs cor range	0.93−1.00

Acknowledgment. The Dirección General de Investigación Científica y Técnica (Proyecto PB94-1445) and the Junta de Andalucía are thanked for financial support. Thanks are also due to the Ministerio de Educación y Ciencia (F.M.A. and T.R.B.) for research fellowships.

Supporting Information Available: Tables giving atomic coordinates, thermal parameters and bond distances, and angles (15 pages). Ordering information is given in any current masthead page.

OM9806500

(32) *TEXSAN-TEXRAY Structure Analysis Package*; Molecular Structure Corporation: The Woodlands, TX, 1985.