°C. Diffraction measurements were carried out at room temperature on a Nonius CAD-4 four-circle diffractometer, using graphite monochromatized Mo Kα radiation. Unit-cell parameters were calculated from the setting angles of 25 carefully centered reflections. Crystal data and intensity collections parameters are given in Table IV. The intensities of three reflections ($\bar{5}20$, $\bar{6}61$, $\bar{4}50$) were monitored every hour of exposure and showed no evidence of decay. For all subsequent computations the Enraf Nonius SPD package was used.[20] Data were corrected for Lorentz polarization but not for absorption. The crystal structure was solved by using the Patterson and Fourier difference methods and refined by full-matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms. The function minimized was $\sum(w|F_o| - |F_c|)^2$, where the weight w is $[4F_o^2]/[\sigma^2(F_o) - (0.07|F_o|^2)]$. Hydrogen atoms were placed in calculated positions (C–H distances = 0.95 Å) in structure factor calculations and were assigned isotropic thermal parameters of B = 5 Å^2, except for H1, H1T, H2, and H2T, which were positioned by Fourier difference and refined isotropically. A final difference map revealed no significant residual peak. Neutral atom scattering factors used for all atoms and anomalous dispersion coefficients were obtained from standard sources.[21] The positional parameters obtained from the last cycle of refinement are listed in Table V, with the corresponding standard deviations.

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Supplementary Material Available: Views of the structure of each molecule of **2a** in the asymmetric unit with the complete labeling scheme (Figure S-1) and a perspective view of the unit cell (Figure S-2), temperature factors for anisotropic atoms (Table S-I), a complete set of bond distances (Table S-II), and a complete set of bond angles (Table S-III) (12 pages); observed and calculated structure factor amplitudes for all observed reflections (Table S-IV) (29 pages). Ordering information is given on any current masthead page.

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(20) Frenz, B. A. In *Computing in Crystallography*; Schenk, H., Olthof-Hazekamp, R., van Koningsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, The Netherlands, 1978; pp 64–71.

(21) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, 1974; Vol. IV, p 99.

Intramolecular Carbon–Carbon vs Carbon–Nitrogen Bond Formation in an Organopalladium Compound[†]

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The reaction of the cyclopalladated compound of the 1,2,3,4-tetrahydro-1-(dimethylamino)naphthalene ligand, **2**, with 1 equiv of ethyl 3-phenylpropynoate leads to insertion of one alkyne into the Pd–C bond of **2**. The depalladation of this compound at reflux chlorobenzene temperature results in the synthesis of organic heterocyclic compounds. In the case of an iodated derivative the complete demethylation of the NMe_2 group is observed concomitantly with the C–N bond formation. The reaction of **2** with 2 equiv of diphenylacetylene leads to insertion of two alkynes into the Pd–C bond. The depalladation of this latter compound affords organic products containing a fulvene or a naphthyl ring via annulation of two phenyl units of the alkyne and an indolizinium derivative generated through intramolecular formation of a C–N bond by nucleophilic addition of an NMe_2 group to a polysubstituted alkene unit η^2-bonded to Pd.

Organopalladium compounds whose Pd–C bond is stabilized by intramolecular chelation of a nitrogen atom have led to interesting reactions with alkynes.[1] Thus, several syntheses of heterocyclic compounds have been observed, the C–N bond being formed by addition of the nitrogen atom to an activated alkene unit.[2] This latter possibility is however hampered by several side reactions that might take place at the alkyne substituents such as the annulation of aryl rings[3a–c] or the formation of pyrones by dealkylation of an ester function.[3d] It has for instance been established that depalladation of organopalladium compounds built up via reactions of the cyclopalladated (dimethylamino)methylphenyl ligand (referred to hereafter as "dmba") with two alkynes per Pd atom invariably led to the formation of organic compounds in which no C–N

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(1) Pfeffer, M. *Recl. Trav. Chim. Pays-Bas* **1990**, *109*, 567.

(2) (a) Maassarani, F.; Pfeffer, M.; Le Borgne, G. *Organometallics* **1987**, *6*, 2029. (b) Wu, G.; Rheingold, A. L.; Heck, R. F. *Organometallics* **1987**, *6*, 2386. (c) Wu, G.; Geib, S. J.; Rheingold, A. L.; Heck, R. F. *J. Org. Chem.* **1988**, *53*, 3238. (d) Pfeffer, M.; Rotteveel, M. A. *Recl. Trav. Chim. Pays-Bas* **1989**, *108*, 317.

(3) (a) Wu, G.; Rheingold, A. L.; Geib, S. J.; Heck, R. F. *Organometallics* **1987**, *6*, 1941. (b) Tao, W.; Silverberg, L. J.; Rheingold, A. L.; Heck, R. F. *Organometallics* **1989**, *8*, 2550. (c) Pfeffer, M.; Rotteveel, M. A.; Sutter, J. P.; De Cian, A.; Fischer, J. *J. Organomet. Chem.* **1989**, *371*, C21. (d) Pfeffer, M.; Rotteveel, M. A.; De Cian, A.; Fischer, J.; Le Borgne, G. *J. Organomet. Chem.* **1991**, *413*, C15.

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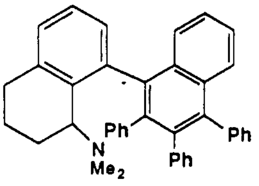
bond has been formed.[3b-d] In this paper we show that by adjusting the conformation of the starting palladated ligand it is possible to form the desired C–N bond, and hence, it is expected that some control upon the reactivity of cyclopalladated compounds can be envisaged in the future.

Results and Discussion

Assuming that the flexibility of the aryl–CH_2 bond of dmba was responsible for the N atom to be remote from the coordination sphere of the Pd center and, thus, for the nonformation of the C–N bond, we chose to investigate the chemistry of the related 1,2,3,4-tetrahydro-1-(dimethylamino)naphthalene ligand, 1, for which this flexibility is much lowered because of the existence of the $-(CH_2)_3-$ chain. Cyclopalladation of 1 to give 2 was readily achieved, and the insertion of one or two alkynes afforded the compounds 3 and 6, as depicted in Scheme I.

Depalladation of compound 3 can be induced by thermal degradation of the corresponding iodo derivative to give the neutral compound 4. A similar reaction, with no demethylation of the NMe_2 unit, however, took place to afford the cationic 5 in the presence of $AgBF_4$ (4 and 5 are obtained in 29 and 17% isolated yields, respectively). It has been observed previously that partial dealkylation of NMe_2 groups can occur in related cyclization reactions in presence of iodide.[2a,4] The analysis of the gaseous product from reaction iii shows that it contains MeI and methane. Whereas the production of iodomethane can be rationalized by a S_N2 reaction of I^- on a cationic derivative analogous to 5 having I^- as a counteranion, the presence of methane is more puzzling and no rational explanation for its formation has yet been found.

High-temperature treatment (ca. 132 °C) of the cationic compound formed by chloride abstraction from 6 by a silver salt led to a mixture of three products. Two of them (7 and 8, total yield 30%, 2:1 ratio) were shown to contain annulated aryl groups by analogy with the dmba work.[3c,d] These two compounds could be obtained with similar yields by treating 6 with an excess (up to 5 equiv) of maleic anhydride. The structure of the third product, obtained in moderate yield (17%), has been determined by a single-crystal X-ray diffraction study.



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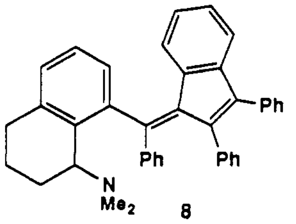

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The cationic part of the molecule is shown in Figure 1. It reveals the presence of two fused heterocyclic units: the depalladation of 6 has thus resulted in the formation of a C–N bond to carbon C12 and of a C–C bond between the formerly palladated carbon atom in 6 and one methyl group of the NMe_2 unit. Thus, 9 can be best described as an indolizinium derivative. The ^1H NMR spectrum of 9 before crystallization revealed that it exits as a single diastereoisomer, indicating that the reaction that has led to its formation is highly stereoselective.

A possible reaction path for the formation of 9 is presented in Scheme II. An early step of the mechanism could be in line with what we proposed earlier to explain the geometry of the diinserted compounds of type 6 where two

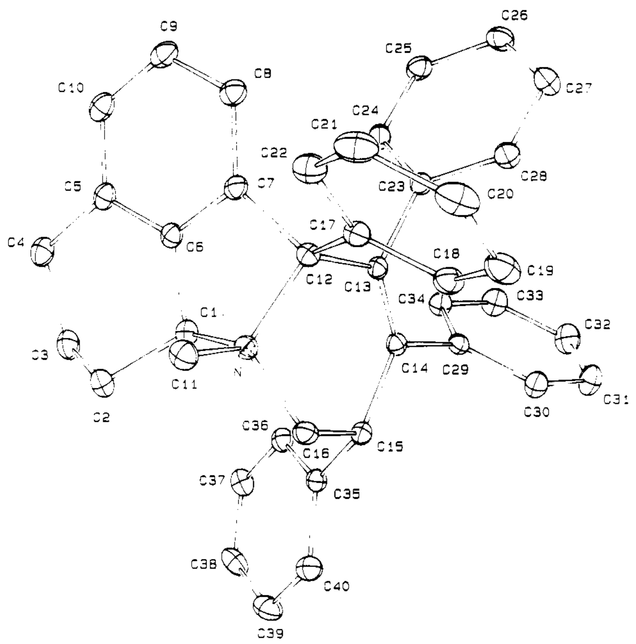
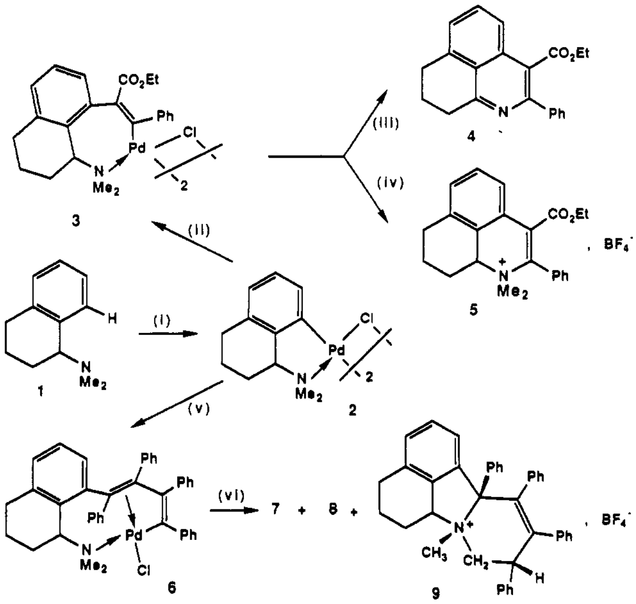


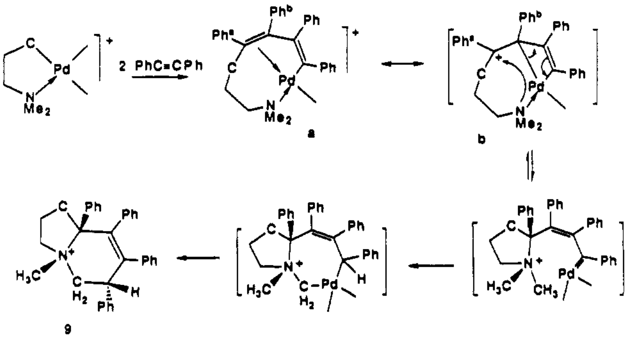
Figure 1. ORTEP view of compound 9. Elipsoids are scaled to include 30% of electronic density; H atoms are omitted for clarity.

Scheme I[a]



[a] Reagents and conditions: (i) Li_2PdCl_4, MeOH: (ii) PhC≡CCO$_2$Et, CH_2Cl_2, 4 h; (iii) (1) NaI, acetone, (2) PhCl reflux, 3 h; (iv) (1) $AgBF_4$, CH_2Cl_2/MeCN, (2) PhCl reflux, 1.5 h; (v) PhC≡CPh, CH_2Cl_2 reflux, 4 h; (vi) (1) $AgBF_4$, CH_2Cl_2/MeCN, (2) PhCl reflux, 2 h, (3) NaOAc, MeOH.

Scheme II. Proposed Reaction Path for the Formation of 9



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[4] Beydoun, N.; Pfeffer, M. *Synthesis* **1990**, 729. Ten Hoedt, R. W. N.; Van Koten, G.; Noltes, J. G. *Synth. Commun.* **1977**, *7*, 61.

phenyl groups are trans with respect to the first alkene unit. We suggested that a metallocyclic flip[5] could occur on the intermediate **a** through which the phenyl group Ph^a is becoming trans to Ph^b.[1,6] The mechanism through which these two aryl rings are then annulated from compound **6** to give **7** and **8**, respectively, should be akin to what was proposed earlier by Heck et al.[3a] and by some of us.[7]

The formation of **9** could occur via **b**, a mesomeric form of **a**. A nucleophilic attack of the NMe$_2$ group at the carbocationic center α to the tetrahydronaphthyl unit should thus produce the heterocyclic five-membered ring present in **9**. We believe, however, that this reaction is only made possible here because of the conformation of the 1,2,3,4-tetrahydro-1-(dimethylamino)naphthalene ligand that forces the N atom to stay close to the butadienyl moiety throughout the process; this is in contrast to what is occurring with the dmba ligand that only leads to annulation reactions of either the aryl rings Ph^a or Ph^b.[3b,c] The final C–C bond could then be formed via a palladacarbene intermediate, which might insert into a C–H bond of a methyl group followed by reductive elimination to afford **9**. Related C–H migrations associated with C–C bond formations have been described recently by Rudler et al. and by Dötz et al. during their studies of the reactivity of chromium carbene complexes.[8]

Experimental Section

General procedures and spectroscopic measurements were performed as described previously.[2a]

Synthesis of 1-(*N*,*N*-Dimethylamino)-1,2,3,4-tetrahydronaphthalene (1). This ligand was made from 1-amino-1,2,3,4-tetrahydronaphthalene with a mixture of formaldehyde and formic acid according to a published procedure[9] in 86% yields. ^{1}H NMR (CDCl$_3$, δ): 7.61–7.02 (m, 4 H, aromatic protons), 3.78–2.32 and 2.24–1.17 (2 m, 7 H, aliphatic protons), 2.27 (s, 6 H, NMe$_2$).

Synthesis of Compound 2. A solution of **1** (5.25 g, 30 mmol) in MeOH (25 mL) was added dropwise to a well-stirred solution of lithium tetrachloropalladate (7.87 g, 30 mmol) in MeOH (60 mL) at room temperature. After 2 h of stirring, during which time an orange precipitate is formed, a solution of NEt$_3$ (4.2 mL, 30 mmol) in MeOH (25 mL) is added slowly (the addition time should take 1 h in order to avoid the reduction of Pd(II)) to the reaction mixture, which is then stirred for 4 h. The yellow precipitate which is thus formed is filtered, washed with water and MeOH, and dissolved in CH$_2$Cl$_2$ (600 mL). This solution is filtered over a Celite column (length = 3 cm), and the solvent is removed in vacuo, affording **2** as a yellow powder, which is washed with pentane and dried in vacuo (8.41 g, 88%). Anal. Calcd for C$_{24}$H$_{32}$Cl$_2$N$_2$Pd$_2$: C, 45.59; H, 5.10; N, 4.43. Found: C, 45.56; H, 5.17; N, 4.32. ^{1}H NMR (CDCl$_3$ + Py-d_5, δ): 7.26–7.20 (m, 2 H, aromatic protons), 6.69 (d, 1 H, aromatic proton, $^3J_{HH}$ = 8.2 Hz), 4.40 (m, 1 H, CHN), 3.03 and 2.63 (2 s, 6 H, N(CH$_3$)$_2$), 2.58–1.12 (m, 6 H, (CH$_2$)$_3$).

Synthesis of Compound 3. A solution of ethyl 3-phenylpropynoate (0.697 g, 4 mmol) in CH$_2$Cl$_2$ (20 mL) is added dropwise to a solution of **2** (1.262 g, 2 mmol) in CH$_2$Cl$_2$ (40 mL). The reaction mixture is stirred at room temperature for 4 h. The deep orange solution thus obtained is filtered on a Celite column (length = 4 cm) to remove any traces of metallic palladium. The solution is concentrated in vacuo (to ca. 20 mL), and addition of *n*-pentane (100 mL) affords compound **3** as a yellow solid (1.81 g, 98%), which may be used as such without further purification. Crystallization in CH$_2$Cl$_2$/hexane affords analytically pure **3**. Anal. Calcd for C$_{46}$H$_{52}$Cl$_2$N$_2$O$_4$Pd$_2$: C, 56.34; H, 5.34; N, 2.86. Found: C, 56.20; H, 5.56; N, 3.07. ^{1}H NMR (CDCl$_3$ + Py-d_5, δ): 7.78–6.74 (m, 8 H, aromatic protons), 4.51 (m, 1 H, CHN), 3.69 (m, ABX$_3$ pattern, 2 H, CH$_2$ of Et), 3.15 and 2.77 (2 s, 6 H, N(CH$_3$)$_2$), 2.68 and 2.14–1.15 (2 m, 6 H, (CH$_2$)$_3$), 0.65 (t, 3 H, CH$_3$ of Et, $^3J_{HH}$ = 7.1 Hz).

Synthesis of Compound 4. An excess of sodium iodide (0.75 g, 5 mmol) is added to a solution of **3** (0.979 g, 1 mmol) in MeOH (50 mL), which is stirred at room temperature for 2 h. The solvent is then removed in vacuo, and the orange residue is washed with water and dried in vacuo, affording quantitatively the corresponding iodide derivative of **3**. A solution of this latter (1.6 g, 1.37 mmol) in chlorobenzene (40 mL) is heated at reflux temperature during 3 h, affording a dark solution from which the solvent is removed in vacuo. Compound **4** is extracted from the black residue with CH$_2$Cl$_2$ (250 mL). Removal of the solvent in vacuo and washing of the residue with *n*-hexane (10 mL) affords **4** as a yellow-green powder (0.260 g, 30%). Anal. Calcd for C$_{21}$H$_{19}$NO$_2$: C, 79.47; H, 6.03; N, 4.41. Found: C, 79.26; H, 6.27; N, 4.81. ^{1}H NMR (CDCl$_3$, δ): 7.88–7.26 (m, 8 H, aromatic protons), 4.20 (q, 2 H, CH$_2$ of Et), 3.35 and 3.18 (2 t, 4 H, 2 CH$_2$), 2.22 (q, 2 H, CH$_2$), 1.01 (t, 3 H, CH$_3$, $^3J_{HH}$ = 7.1 Hz). Mass spectrum: m/z 317 (M$^+$), 288 (M$^+$ – Et), 272 (M$^+$ – OEt), 244 (M$^+$ – CO$_2$Et).

Synthesis of Compound 5. A solution of silver tetrafluoroborate (0.39 g, 2 mmol) in CH$_2$Cl$_2$/MeCN (15 mL/1.5 mL) is added to a solution of **3** (0.979 g, 1 mmol) in CH$_2$Cl$_2$ (15 mL). AgCl is eliminated by filtration over a Celite column (length = 4 cm), and removal of the solvent in vacuo affords an oil, which gives the cationic derivative of **3** upon washing with *n*-pentane as a pale orange powder. A solution of the latter (1.76 g, 2.82 mmol) in chlorobenzene (35 mL) is heated at reflux temperature during 1.5 h. The black residue that is obtained after removal of the solvent is put on the top of an alumina column. Elution with CH$_2$Cl$_2$ affords an oil, which we could not characterize; elution with acetone (150 mL) gives **5** as white microcrystals after removal of the solvent (0.204 g, 17%). The same compound could be made by treating **2** with AgBF4 followed by reaction with 1 equiv of ethyl 3-phenylpropynoate in PhCl at relfuxing temperature in lower yields, however. Anal. Calcd for C$_{23}$H$_{26}$BF$_4$NO$_2$: C, 63.47; H, 6.02; N, 3.12. Found: C, 63.62; H, 6.35; N, 3.15. ^{1}H NMR (CDCl$_3$, δ): 7.59–7.17 (m, 8 H, aromatic protons), 5.52 (m, 1 H, CHN), 3.98 (q, 2 H, CH$_2$ of Et), 3.10 (s, 6 H, N(CH$_3$)$_2$), 2.95–2.70 and 2.32–1.88 (2 m, 6 H, (CH$_2$)$_3$), 0.85 (t, 3 H, CH$_3$ of Et, $^3J_{HH}$ = 7.1 Hz). Mass spectrum: m/z 348 (M$^+$), 347 (M$^+$ – H).

Synthesis of Compound 6. Diphenylacetylene (0.358 g, 2 mmol) is added to a solution of **2** (0.315 g, 0.5 mmol) in CH$_2$Cl$_2$ (25 mL). The mixture is heated at reflux during 4 h. The orange solution thus obtained is filtered on a Celite column (length = 4 cm) to remove traces of metallic Pd, and the solvent is removed in vacuo. The residue is washed with *n*-pentane (50 mL) and then dissolved in the minimum amount of CH$_2$Cl$_2$. Compound **6** is obtained as yellow crystals through addition of *n*-pentane (0.526 g, 79%). Anal. Calcd for C$_{40}$H$_{36}$ClNPd: C, 71.43; H, 5.40; N, 2.08. Found: C, 71.07; H, 5.56; N, 2.39. ^{1}H NMR (CDCl$_3$, δ): 8.31–6.51 (m, 23 H, aromatic protons), 3.20 (m, 1 H, CHN), 2.98 and 2.30 (2 s, 6 H, N(CH$_3$)$_2$), 2.62 and 1.72–0.77 (2 m, 6 H, (CH$_2$)$_3$).

Synthesis of Compounds 7 and 8. An excess of maleic anhydride (0.784 g, 8 mmol) is added to a solution of **6** (1 g, 1.49 mmol) in chlorobenzene (45 mL), and the mixture is refluxed during 2 h. The solution is pumped dry, and the residue is placed on an alumina column (length = 10 cm). Elution with CH$_2$Cl$_2$ (200 mL) affords, after removal of the sovent, a mixture of **7** and **8** as an orange powder (0.4 g, 50%). By fractional crystallization in CH$_2$Cl$_2$/*n*-pentane **7** and **8** can be separated as yellow and deep orange crystals, respectively, in a 2:1 ratio. Anal. Calcd for C$_{40}$H$_{35}$N: C, 90.56; H, 6.80; N, 2.64. Found: C, 90.78; H, 6.89; N, 2.64. ^{1}H NMR for **7** (CDCl$_3$, δ): 7.78–6.49 (m, 22 H, aromatic protons), 3.88 (m, 1 H, CHN), 2.47–1.97 and 1.60–1.25 (2 m, 6 H, (CH$_2$)$_3$), 1.93 (s, 6 H, NMe$_2$). Mass spectrum for **7**: m/z 529 (M$^+$). ^{1}H NMR for **8** (CDCl$_3$, δ): 7.57–6.60 (m, 22 H, aromatic protons), 2.95–2.64 and 1.90–1.25 (2 m, 7 H, (CH$_2$)$_3$ + CHN), 1.91

---

(5) Taylor, S. A.; Maitlis, P. M. *J. Am. Chem. Soc.* **1978**, *100*, 4700.

(6) Dupont, J.; Pfeffer, M.; Daran, J. C.; Gouteron, J. *J. Chem. Soc., Dalton Trans.* **1988**, 2421.

(7) Dupont, J.; Pfeffer, M.; Rotteveel, M. A.; De Cian, A.; Fischer, J. *Organometallics* **1989**, *8*, 1116. Dupont, J.; Pfeffer, M.; Theurel, L.; Rotteveel, M. A.; De Cian, A.; Fischer, J. *New J. Chem.* **1991**, *15*, 551. Pfeffer, M.; Rotteveel, M. A.; Sutter, J. P. Manuscript in preparation.

(8) Dötz, K. H.; Schäfer, T.; Harns, K. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 176. Dötz, K. H.; Erben, H. G.; Harms, K. *J. Chem. Soc., Chem. Commun.* **1989**, 692. Audouin, M.; Blandiniere, S.; Parlier, A.; Rudler, H. *J. Chem. Soc., Chem. Commun.* **1990**, 23.

(9) Van Koten, G.; Jastrzebski, J. T. B. H.; Noltes, J. G.; Pontenagel, W. M. G. F.; Kroon, J.; Spek, A. L. *J. Am. Chem. Soc.* **1978**, *100*, 5021.

Table I. Bond Distances in Angstroms[a]

C1–C2	1.519 (2)	C18–C19	1.388 (2)
C1–C6	1.482 (2)	C19–C20	1.384 (3)
C1–N	1.531 (2)	C20–C21	1.374 (3)
C2–C3	1.539 (3)	C21–C22	1.389 (3)
C3–C4	1.540 (3)	C23–C24	1.390 (2)
C4–C5	1.501 (3)	C23–C28	1.388 (2)
C5–C6	1.383 (2)	C24–C25	1.381 (2)
C5–C10	1.392 (2)	C25–C26	1.386 (3)
C6–C7	1.375 (2)	C26–C27	1.381 (3)
C7–C8	1.388 (2)	C27–C28	1.381 (2)
C7–C12	1.525 (2)	C29–C30	1.388 (2)
C8–C9	1.394 (3)	C29–C34	1.384 (2)
C9–C10	1.388 (3)	C30–C31	1.384 (3)
N–C11	1.507 (2)	C31–C32	1.374 (3)
N–C12	1.589 (2)	C32–C33	1.380 (3)
N–C16	1.507 (2)	C33–C34	1.389 (2)
C12–C13	1.545 (2)	C35–C36	1.385 (2)
C12–C17	1.512 (2)	C35–C40	1.396 (2)
C13–C14	1.334 (2)	C36–C37	1.390 (2)
C13–C23	1.500 (2)	C37–C38	1.379 (3)
C14–C15	1.511 (2)	C38–C39	1.381 (3)
C14–C29	1.501 (2)	C39–C40	1.384 (3)
C15–C16	1.527 (2)	B–F1	1.378 (2)
C15–C35	1.536 (2)	B–F2	1.375 (2)
C17–C18	1.390 (2)	B–F3	1.384 (2)
C17–C22	1.396 (2)	B–F4	1.391 (2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table II. Bond Angles in Degrees[a]

C2–C1–C6	112.0 (1)	N–C16–C15	114.1 (1)
C2–C1–N	120.1 (1)	C12–C17–C18	120.8 (2)
C6–C1–N	101.7 (1)	C12–C17–C22	120.6 (2)
C1–C2–C3	104.5 (1)	C18–C17–C22	118.5 (2)
C2–C3–C4	113.0 (2)	C17–C18–C19	120.8 (2)
C3–C4–C5	113.0 (1)	C18–C19–C20	119.9 (2)
C4–C5–C6	119.2 (2)	C19–C20–C21	119.8 (2)
C4–C5–C10	124.7 (2)	C20–C21–C22	120.6 (2)
C6–C5–C10	116.0 (2)	C17–C22–C21	120.3 (2)
C1–C6–C5	124.5 (2)	C13–C23–C24	120.5 (1)
C1–C6–C7	111.6 (1)	C13–C23–C28	120.8 (1)
C5–C6–C7	123.9 (2)	C24–C23–C28	118.6 (2)
C6–C7–C8	119.8 (2)	C23–C24–C25	120.8 (2)
C6–C7–C12	109.8 (1)	C24–C25–C26	120.2 (2)
C8–C7–C12	130.2 (2)	C25–C26–C27	119.1 (2)
C7–C8–C9	117.5 (2)	C26–C27–C28	120.8 (2)
C8–C9–C10	121.6 (2)	C23–C28–C27	120.4 (2)
C5–C10–C9	121.1 (2)	C14–C29–C30	119.6 (2)
C1–N–C11	110.0 (1)	C14–C29–C34	122.0 (2)
C1–N–C12	102.9 (1)	C30–C29–C34	118.3 (2)
C1–N–C16	114.2 (1)	C29–C30–C31	120.2 (2)
C11–N–C12	110.9 (1)	C30–C31–C32	121.2 (2)
C11–N–C16	107.4 (1)	C31–C32–C33	119.2 (2)
C12–N–C16	111.5 (1)	C32–C33–C34	119.7 (2)
C7–C12–N	99.2 (1)	C29–C34–C33	121.3 (2)
C7–C12–C13	108.2 (1)	C15–C35–C36	124.2 (2)
C7–C12–C17	117.3 (1)	C15–C35–C40	117.8 (2)
N–C12–C13	107.8 (1)	C36–C35–C40	118.0 (2)
N–C12–C17	110.3 (1)	C35–C36–C37	121.3 (2)
C13–C12–C17	113.0 (1)	C36–C37–C38	119.9 (2)
C12–C13–C14	125.4 (1)	C37–C38–C39	119.5 (2)
C12–C13–C23	113.8 (1)	C38–C39–C40	120.5 (2)
C14–C13–C23	120.7 (1)	C35–C40–C39	120.7 (2)
C13–C14–C15	123.5 (2)	F1–B–F2	110.6 (2)
C13–C14–C29	120.0 (1)	F1–B–F3	109.3 (2)
C15–C14–C29	116.2 (1)	F1–B–F4	107.8 (2)
C14–C15–C16	112.5 (1)	F2–B–F3	110.3 (2)
C14–C15–C35	115.8 (1)	F2–B–F4	110.2 (2)
C16–C15–C35	112.3 (1)	F3–B–F4	108.6 (2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table III. Positional Parameters and *B* Values and Their Estimated Standard Deviations

atom	*x*	*y*	*z*	*B*,[a] Å^2
C1	0.3934 (1)	0.2419 (2)	0.6246 (3)	2.70 (6)
C2	0.3196 (1)	0.2181 (2)	0.5906 (3)	3.45 (6)
C3	0.2813 (1)	0.2984 (2)	0.5723 (3)	3.74 (7)
C4	0.2895 (1)	0.3479 (2)	0.7094 (3)	3.72 (7)
C5	0.3605 (1)	0.3483 (2)	0.7885 (3)	2.92 (6)
C6	0.4071 (1)	0.2961 (2)	0.7484 (3)	2.59 (5)
C7	0.4722 (1)	0.2882 (2)	0.8187 (3)	2.60 (5)
C8	0.4949 (1)	0.3361 (2)	0.9352 (3)	3.09 (6)
C9	0.4495 (1)	0.3908 (2)	0.9760 (3)	3.45 (6)
C10	0.3834 (1)	0.3959 (2)	0.9058 (3)	3.40 (6)
N	0.4477 (1)	0.1776 (1)	0.6633 (2)	2.48 (4)
C11	0.4247 (1)	0.1165 (2)	0.7605 (3)	3.15 (6)
C12	0.5100 (1)	0.2276 (2)	0.7427 (3)	2.51 (5)
C13	0.5417 (1)	0.2728 (2)	0.6300 (3)	2.31 (5)
C14	0.5306 (1)	0.2567 (2)	0.4920 (3)	2.34 (5)
C15	0.4887 (1)	0.1867 (2)	0.4275 (3)	2.52 (5)
C16	0.4656 (1)	0.1329 (2)	0.5386 (3)	2.64 (6)
C17	0.5594 (1)	0.1727 (2)	0.8331 (3)	2.69 (6)
C18	0.6078 (1)	0.1307 (2)	0.7754 (3)	2.94 (6)
C19	0.6495 (1)	0.0754 (2)	0.8552 (3)	3.55 (6)
C20	0.6436 (2)	0.0621 (2)	0.9947 (3)	3.87 (7)
C21	0.5968 (2)	0.1043 (2)	1.0539 (3)	3.90 (7)
C22	0.5545 (1)	0.1593 (2)	0.9743 (3)	3.29 (6)
C23	0.5889 (1)	0.3388 (2)	0.6887 (3)	2.41 (5)
C24	0.5646 (1)	0.4157 (2)	0.7053 (3)	2.95 (6)
C25	0.6082 (1)	0.4777 (2)	0.7522 (3)	3.31 (6)
C26	0.6769 (1)	0.4638 (2)	0.7858 (3)	3.62 (6)
C27	0.7012 (1)	0.3875 (2)	0.7692 (3)	3.62 (7)
C28	0.6578 (1)	0.3255 (2)	0.7215 (3)	3.00 (6)
C29	0.5663 (1)	0.3040 (2)	0.3942 (3)	2.47 (5)
C30	0.6145 (1)	0.2668 (2)	0.3288 (3)	3.17 (6)
C31	0.6499 (1)	0.3105 (2)	0.2535 (3)	3.98 (7)
C32	0.6390 (1)	0.3913 (2)	0.2225 (3)	4.04 (7)
C33	0.5906 (1)	0.4288 (2)	0.2853 (3)	3.77 (7)
C34	0.5544 (1)	0.3850 (2)	0.3700 (3)	3.09 (6)
C35	0.4310 (1)	0.2072 (2)	0.3065 (3)	2.54 (5)
C36	0.4006 (1)	0.2818 (2)	0.2872 (3)	2.89 (6)
C37	0.3447 (1)	0.2945 (2)	0.1829 (3)	3.44 (6)
C38	0.3197 (1)	0.2327 (2)	0.0939 (3)	4.05 (7)
C39	0.3508 (2)	0.1586 (2)	0.1088 (3)	4.08 (7)
C40	0.4058 (1)	0.1457 (2)	0.2140 (3)	3.34 (6)
B	0.3276 (2)	−0.0375 (2)	0.5406 (3)	3.16 (7)
F1	0.33050 (8)	0.0217 (1)	0.4419 (2)	4.40 (4)
F2	0.29215 (9)	−0.1026 (1)	0.4796 (2)	4.82 (4)
F3	0.29746 (8)	−0.0072 (1)	0.6486 (2)	5.46 (4)
F4	0.39336 (8)	−0.0597 (1)	0.5961 (2)	4.62 (4)

[a] *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

(s, 6 H, NMe_2). Mass spectrum for **8**: *m/z* 529 (M^+).

Synthesis of Compound 9. The in situ chloride abstraction from compound **6** (1.354 g, 2 mmol) with $AgBF_4$ is made via the procedure described for compound **5**. This cationic compound is refluxed in chlorobenzene (2 h); the solution is pumped dry, and the organic residue is dissolved in CH_2Cl_2. This solution is filtered through Celite and dried under vacuum; in order to remove the ammonium salts that might have been formed, the orange powder thus formed is washed with *n*-pentane and dissolved in MeOH (50 mL), to which a large excess of sodium acetate is added with vigorous stirring during 15 h. The residue obtained after removal of the solvent is washed with water and dried under vacuum. Extraction with diethyl ether affords compounds **7** and **8** (0.336 g, 32%) in the same ratio as the previous procedure. Compound **9**, which is unsoluble in Et_2O, is obtained as a white powder (0.133 g, 11%). Crystals suitable for an X-ray analysis were obtained via slow diffusion of *n*-hexane into a saturated solution of **9** in CH_2Cl_2. Anal. Calcd for $C_{40}H_{36}BF_4N$: C, 77.79; H, 5.83; N, 2.26. Found: C, 75.88; H, 7.20; N, 2.03. (Despite several recrystallizations no better analyses could be obtained for this compound.) ^1H NMR ($CDCl_3$): 8.24–6.26 (m, 23 H, aromatic protons), 5.80 (dd, 1 H, HC1), 5.07 (m, 1 H, HC15), 4.48 and 4.32 (2 m, 2 H, H_2C16), 2.87 and 2.73 (2 m, 2 H, H_2C3), 2.29 (s, 3 H, NMe), 1.52 and 1.37 (2 m, 2 H, H_2C2) (the assignment of the H resonances of **9** was made with the help of a 2D COSY NMR spectrum in CD_2Cl_2 at 400.13 MHz). Mass spectrum: *m/z* 530 (M^+), 529 ($M^+ - H$), 515 ($M^+ - Me$).

Crystal Structure of 9. Crystal data are as follows: monoclinic; space group $P2_1/n$; a = 20.125 (5), b = 16.679 (4), c = 9.616 (3) Å; β = 99.76 (2)°; V = 3181.0 Å^3, Z = 4; ρ_{calcd} = 1.289 gcm^{-3}; λ = 1.5418 Å; μ = 7.049 cm^{-1}; 4136 independent data collected (Phillips PW 1100/16 diffractometer, $\theta/2\theta$ flying step scan, 3° < θ < 53°) at −100 °C using a local-built gas-flow device. The structure was solved by using MULTAN[10] and refined by full-matrix least squares by using 2873 observed reflections ($I > 3\sigma(I)$). The hydrogen atoms were introduced in structure factor calculations at their computed coordinates (C–H = 0.95 Å, B(H) = 1.3B_{eqv}(C) Å^2) but not refined. No absorption corrections were applied since face indexation was not possible under the cold gas stream and in view of the small absorption coefficient. A final difference map revealed no significant maxima. The scattering factor coefficients come from ref 11. $R(F)$ = 0.035; $R_W(F)$ = 0.036. Crystal data are listed in Tables I–III.

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Supplementary Material Available: Tables of positional parameters of the hydrogen atoms and anisotropic thermal parameters for 9 (4 pages); a listing of observed and calculated structure factors for 9 (11 pages). Ordering information is given on any current masthead page.

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[10] Germain, G.; Main, P.; Woolfson, M. M. *Acta Crytallogr.* 1970, *B26*, 274; 1971, *A27*, 368.

[11] Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2b and 2.3.1.

Metal–Hydride Alkynyl → Metal–Vinylidene Rearrangements Occurring in both Solid State and Solution. Role of the 1-Alkyne Substituent in Determining the Relative Stability of π-Alkyne, Hydride Alkynyl, and Vinylidene Forms at Cobalt

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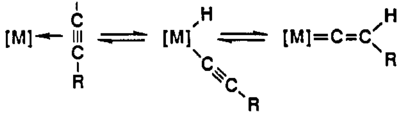
The 16-electron fragment $[(PP_3)Co]^+$ obtained in situ from the dinitrogen complex $[(PP_3)Co(N_2)]BPh_4$ (2) reacts in tetrahydrofuran with terminal alkynes, HC≡CR, yielding π-alkyne adducts of the type $[(PP_3)Co(\pi\text{-}HC{\equiv}CR)]^+$ and vinylidene complexes $[(PP_3)Co\{C{=}C(H)R\}]^+$ as kinetic and thermodynamic products, respectively (R = H, Ph, n-C_3H_7, n-C_5H_{11}, CMe_3, $SiMe_3$; $PP_3 = P(CH_2CH_2PPh_2)_3$). Between the π-alkyne and vinylidene forms, the system evolves through a third species, namely the Co(III) hydride alkynyl complexes $[(PP_3)Co(H)(C{\equiv}CR)]^+$, which are thermodynamically favored over the π-alkyne complexes and disfavored over the vinylidene ones. The sequence $Co(\pi\text{-}HC{\equiv}CR) \rightarrow Co(H)(C{\equiv}CR) \rightarrow Co\{C{=}C(H)R\}$ is controlled by the temperature, so that by a judicious choice of this parameter it is possible to freeze the reactions at any of the three steps. Spectroscopic evidence is provided for the formation of the π-alkyne adducts whereas both the hydride alkynyl and vinylidene complexes have been isolated in the solid state and completely characterized by spectroscopic and X-ray diffraction techniques. The conversion of the hydride alkynyl complexes to the vinylidene isomers is affected inter alia by the nature of the alkyne substituent. In particular, the temperature at which the conversion occurs increases in the order $SiMe_3 > Ph > H \gg CMe_3 > n\text{-}C_3H_7 \cong n\text{-}C_5H_{11}$. Accordingly, the electronic effects seem to prevail over the steric ones in governing the tautomeric rearrangement. Kinetic and thermodynamic studies show that (i) the hydride alkynyl to vinylidene rearrangement is first order in the Co(III) hydride alkynyl complexes and (ii) the rearrangement most likely proceeds via a dissociative intramolecular 1,3-hydrogen shift pathway. The hydride alkynyl to vinylidene rearrangement occurs also in the solid state at relatively low temperatures (from 303 K for R = CMe_3 to 363 K for R = $SiMe_3$) and depends again on the nature of the 1-alkyne terminal substituent.

Introduction

Scheme I



The 1-alkyne to vinylidene tautomerization (Scheme I) occurs widely throughout organometallic chemistry,[1] homogeneous and heterogeneous catalysis,[2] and biochemistry.[3] In recent years, much has been learned about the mechanism of this important reaction, which can be pro-

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[1] For leading references on this subject see: (a) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* 1983, *22*, 59. (b) Senn, D. R.; Wong, A.; Patton, A. T.; Marsi, M.; Strouse, C. E.; Gladysz, J. C. *J. Am. Chem. Soc.* 1988, *110*, 6096. (c) Schubert, U.; Grönen, J. *Chem. Ber.* 1989, *122*, 1237. (d) Adams, J. S.; Bitcon, C.; Brown, J. R.; Collison, D.; Cunningham, M.; Whiteley, M. W. *J. Chem. Soc., Dalton Trans.* 1987, 3049. (e) Birdwhistell, K. R.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* 1985, *107*, 4474. (f) Boland-Lussier, B. E.; Churchill, M. R.; Hughes, R. P.; Rheingold, A. L. *Organometallics* 1982, *1*, 628. (g) Adams, R. D.; Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* 1979, *101*, 7232. (h) Höhn, A.; Werner, H. *J. Organomet. Chem.* 1990, *382*, 255. (i) Antonova, A. B.; Ioganson, A. A. *Russ. Chem. Rev. (Engl. Transl.)* 1989, *58*, 693; *Usp. Khim.* 1989, *58*, 1197. (j) Miller, D. C.; Angelici, R. J. *Organometallics* 1991, *10*, 79.

[2] (a) Landon, S. J.; Shulman, P. M.; Geoffroy, G. L. *J. Am. Chem. Soc.* 1985, *107*, 6739. (b) Katz, T. J.; Ho, T.-H.; Shih, N.-Y.; Ying, Y.-C.; Stuart, V. I. W. *J. Am. Chem. Soc.* 1984, *106*, 2659. (c) Sasaki, Y.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* 1986, 790. (d) Mahé, R.; Sasaki, Y.; Bruneau, C.; Dixneuf, P. H. *J. Org. Chem.* 1989, *54*, 1518. (e) Trost, B. M.; Dyker, G.; Kulawiec, R. J. *J. Am. Chem. Soc.* 1990, *112*, 7809.