ORGANOMETALLICS

Reactivity of cyclopalladated compounds. Part 12. Insertion of 3,3-dimethylcyclopropenes into the palladium-carbon bond of cyclopalladated dimethylbenzylamine, leading to carbon-carbon bond cleavage or cyclopropyl ring retention. X-ray crystal and molecular structure of [cyclic][Pd[C(CO2Me)CMe2CHC6H4CH2NMe2]pyCl]

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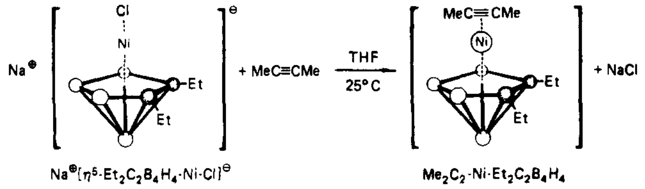
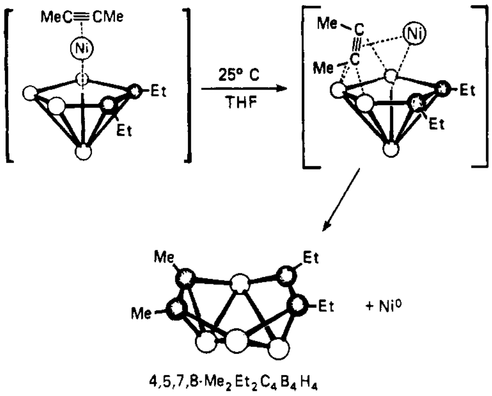
While the mechanism of reaction has not yet been proven, the above observations suggest that the reaction may involve the formation of a nickelacarborane complex, such as shown below, which upon warming can intramolecularly eliminate NaCl and react with 2-butyne to generate an alkyne/metallacarborane intermediate.



Upon standing this alkyne/nickelacarborane complex could then undergo reductive cycloaddition to form the four-carbon carborane and nickel metal:



Fehlner[11,12] first synthesized the carborane 4,5,7,8-$Me_4C_4B_4H_4$ in 60% yield from the photolytic reaction of $B_4H_8Fe(CO)_3$ and 2-butyne; however, this synthesis is limited by the difficult, low-yield (10–20%), synthesis of the ferraborane $B_4H_8Fe(CO)_3$. The peralkylated derivative has also been prepared[13] by El-Essawi and Siebert in 30% yield by treating 2,3,5-thiadiborolene with 2 equiv of potassium metal.

The carborane synthesis described here has several significant advantages over those previously reported. The reaction involves a convenient "one-pot" procedure and employs the readily accessible[14] 2,3-$Et_2C_2B_4H_6$ as a starting material. Furthermore, the product is easily isolated in high purity by simple vacuum-line fractionation.

The above results are important, not only because they provide a reasonable synthetic route to the *nido*-$R_4C_4B_4H_4$ carborane system but also because they suggest that metal reagents may be able to promote two-carbon insertions into a variety of polyhedral boron cage systems leading to new routes to two, four, and, perhaps, higher carbon carborane clusters. We are continuing to study both the scope of these reactions and the chemistry of the unique hybrid "organic–inorganic" cluster *nido*-$R_4C_4B_4H_4$.

Acknowledgment. We thank the National Science Foundation and the Army Research Office for the support of this work.

Registry No. *nido*-2,3-$Et_2C_2B_4H_6$, 80583-48-8; MeC≡CMe, 503-17-3; $NiCl_2$, 7718-54-9; *nido*-4,5,7,8-$Me_2Et_2C_4B_4H_4$, 102493-34-5.

Insertion of 3,3-Dimethylcyclopropenes into the Pd–C Bond of Cyclopalladated Dimethylbenzylamine,[1] Leading to C–C Bond Cleavage or Cyclopropyl Ring Retention. X-ray Crystal and Molecular Structure of [Pd{C(CO₂Me)CMe₂CHC₆H₄CH₂NMe₂}pyCl]

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Summary: When 3,3-dimethylcyclopropenes $CR^1{=}CR^2CMe_2$ (where R^1, R^2 = H, CO_2Me) are allowed to react with the complex $[\{Pd(C_6H_4CH_2NMe_2)(\mu\text{-}Cl)\}_2]$ (**1**), insertion into the Pd–C bond of the cyclopalladated dimethylbenzylamine (dmba) takes place to give two types of compound. Opening of the strained ring of the olefin affords monomeric $[Pd\{(\eta^3\text{-}CMe_2\cdots CR^2\cdots CR^1)C_6H_4CH_2NMe_2\}Cl]$ (**2**), whereas simple insertion without C–C bond cleavage leads to dimeric $[\{Pd(CR^1CMe_2CR^2C_6H_4CH_2NMe_2)(\mu\text{-}Cl)\}_2]$ (**3**), in which the cyclopropyl ring is bonded to both the dmba moiety and the Pd atom. With 3,3-dimethylcyclopropene itself (R^1 = R^2 = H) only compound **2a** is obtained, whereas 1,2-dicarbomethoxy-3,3-dimethylcyclopropene (R^1 = R^2 = CO_2Me) affords only compound **3a**. However, the cyclopropene where R^1 = H and R^2 = CO_2Me gives a mixture of both **2b** and **3b** in a 1:1 ratio. Compounds **3** react with pyridine in a bridge-splitting reaction to give the monomers **4a** and **4b**, the latter being fully characterized by an X-ray diffraction study. Crystals of $[Pd\{C(CO_2Me)CMe_2CHC_6H_4CH_2NMe_2\}pyCl]$ (**4b**) belong to the space group $P2_12_12_1$ with a = 12.408 (5) Å, b = 16.315 (4) Å, c = 10.423 (5) Å, v = 2109.9 Å^3, and Z = 4. The structure has been refined to R = 0.028 and R_w = 0.038. The pyridine is located trans to the nitrogen atom of the dmba. The cyclopropyl unit is σ-bonded to Pd via the carbon atom which bears the CO_2Me group whereas its CH group is bonded to the previously metalated carbon atom of the dmba. The geometry of the new seven-membered organometallic ring compares favorably with that of related compounds obtained by insertion of alkynes into the Pd–C bond of cyclopalladated dmba.

It has been shown that cyclopropenes display versatile behavior toward transition-metal complexes. Indeed, it

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(10) ^{11}B NMR (115.5 MHz, ppm, CH_2Cl_2, C_6D_6): −11.1 (d, 2), −12.5 (d, 1), −12.9 (d, 1). ^1H NMR (200 MHz, δ, C_6D_6): 1.02 (t, 6), 1.88 (s, 6), 2.30 (m, 4). Mass spectrum: cutoff at *m/e* 184, corresponding to $C_{10}H_{20}B_4$.

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[1] Reactivity of cyclopalladated compounds. Part 12. Part 11: Arlen, C.; Pfeffer, M.; Bars, O.; Le Borgne, G. *J. Chem. Soc., Dalton Trans.* **1986**, 359.

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has been reported to date that their three-membered rings can either be maintained or can be cleaved in a variety of ways during these reactions. Examples of the former mode of reaction include those in which the cyclopropene moiety is found as a simple olefin π-coordinated to the metal[3] or in which it takes part in oligomerization reactions[4] through the olefinic bond via metallacycloalkane complexes. In the latter mode of reaction, treatment with transition-metal complexes can afford η^3-allylic[5] or η^4-vinylketene[6] ligands via the cleavage of one carbon–carbon single bond; the rupture of the olefinic bond has also been reported at a dirhodium center.[7]

It has long been recognized that cyclopropenes have properties intermediate between those of alkenes and alkynes;[8] to our knowledge, however, no reactions of these reagents with metal–alkyl or metal–aryl complexes have yet been reported. We have already shown that substituted alkynes react readily with cyclopalladated amines, leading to metallocyclic enlargement by insertion of one or two alkyne molecules into their Pd–C bonds.[9] We have, therefore, explored the reactivity of cyclopropenes with the cyclopalladated dimethylbenzylamine dimer **1** hoping that the presence of the N donor atom would stabilize the new organometallic species thus formed.

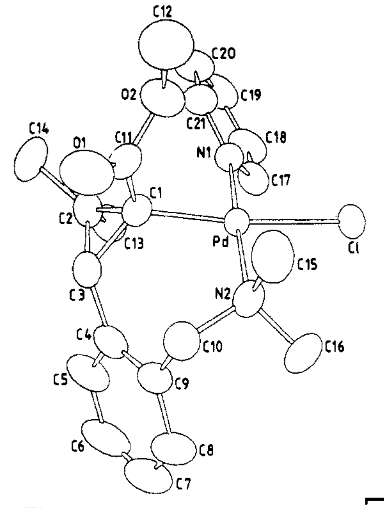

Figure 1. The molecular structure of [Pd{C(CO$_2$Me)CMe$_2$CHC$_6$H$_4$CH$_2$NMe$_2$}(C$_5$H$_5$N)Cl] (**4b**). Relevant bond lengths (Å) and angles (deg) are as follows: Pd–N1 = 2.063 (3); Pd–N2 = 2.126 (3); Pd–C1 = 2.045 (3); Pd–Cl = 2.405 (1); C1–C2 = 1.534 (4); C2–C3 = 1.506 (5); C3–C1 = 1.502 (5); C3–C4 = 1.490 (5); N2–Pd–C1 = 91.3 (1); C1–C3–C4 = 120.2 (3); C1–C3–C2 = 61.3 (2); C3–C2–C1 = 59.2 (2); C2–C1–C3 = 59.5 (2); Pd–C1–C3 = 124.3 (2).

A mixture of 3,3-dimethylcyclopropene (in large excess) and compound **1** in refluxing CH$_2$Cl$_2$ affords, after several hours, a new organometallic compound, **2a**, as yellow crystals in low to moderate yield.[10] The ^{1}H NMR spectrum shows that both the NMe$_2$ and the CH$_2$ moieties of the dmba are diastereotopic, suggesting that no plane of symmetry is present in the complex and, therefore, that insertion of the cyclopropene into the Pd–C bond of **1** has taken place. Accordingly, the two methyls of the cyclopropene are inequivalent. The chemical shifts of the olefinic protons of the cyclopropene are good evidence that a carbon–carbon single bond of the cycloalkene has been broken during the insertion reaction, this moiety being now η^3-bonded to Pd.[12] This leads to a new allylic ligand[13] which is internally coordinated to the palladium via the nitrogen atom of the dmba.

In order to improve the yields of the products, we have investigated the chemistry of carbomethoxy-substituted cyclopropenes (which are known to have increased thermal stability) toward the cyclopalladated complex **1**.

Two equivalents of 1-carbomethoxy-3,3-dimethylcyclopropene react with **1** during 20 h in refluxing CH$_2$Cl$_2$ to give a mixture of compounds **2b** and **3b**, both in reasonable yield. These products are separated by fractional crys-

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(10) Compound **2a** was synthesized by using a 10-fold excess of 3,3-dimethylcyclopropene with **1**. The mixture was refluxed in CH$_2$Cl$_2$ for 6 h, the reaction flask being equipped with a dry ice/acetone cooled condenser. Unfortunately, the separation of **2a** from unreacted **1** was not possible since crystallization from a toluene/pentane solution always afforded yellow crystals consisting of a 1:1 mixture of these two compounds. Anal. Calcd for C$_{20.2}$H$_{26.8}$NO$_2$PdCl (**2b** + 0.6 toluene): C, 53.03; H, 5.86; N, 3.06. Found: C, 53.02; H, 5.89; N, 3.40. Anal. Calcd for C$_{18.33}$H$_{24.66}$NO$_2$PdCl (**3b** + $^1/_3$ toluene): C, 50.82; H, 5.69; N, 3.23. Found: C, 51.04; H, 5.66; N, 3.19. Anal. Calcd for C$_{21}$H$_{27}$ClN$_2$O$_2$Pd (**4b**): C, 52.40; H, 5.61; N, 5.82. Found: C, 51.91; H, 5.37; N, 5.79. Anal. Calcd for C$_{18}$H$_{24}$ClNO$_4$Pd (**3a**): C, 46.96; H, 5.22; N, 3.04. Found: C, 46.63; H, 5.19; N, 3.32. Anal. Calcd for C$_{23.5}$H$_{30}$Cl$_2$N$_2$O$_4$Pd (**4a** + 0.5CH$_2$Cl$_2$): C, 48.50; H, 5.16; N, 4.81. Found: C, 48.44; H, 5.15; N, 4.59.

(11) ^{1}H NMR (200 MHz, CDCl$_3$, 20 °C): **2a**, δ 5.25 and 4.66 (2d, 2 H, allylic protons H^a and H^b (see text), $^3J_{H-H}$ = 10.9 Hz), 3.98 and 3.16 (2d, 2 H, CH$_2$, $^2J_{HA-HB}$ = 11.9 Hz), 3.03 (s, 3 H, NCH$_3$), 2.08 (s, 3 H, NCH$_3$), 1.64 (s, 3 H, CH$_3$), 1.43 (s, 3 H, CH$_3$); **2b**, δ 4.78 (s, 1 H, allylic proton), 3.48 (s, 3 H, CO$_2$CH$_3$), 3.23 and 4.09 (2d, 2 H, CH$_2$, $^2J_{HA-HB}$ = 12.4 Hz), 3.01 (s, 3 H, NCH$_3$), 2.18 (s, 3 H, NCH$_3$), 1.54 (s, 3 H, CH$_3$), 1.43 (s, 3 H, CH$_3$); **4b**, δ 4.97 and 2.59 (2d, 2 H, CH$_2$, $^2J_{HA-HB}$ = 11.7 Hz), 3.86 (s, 3 H, CO$_2$CH$_3$), 2.94 (s, 3 H, NCH$_3$), 2.81 (s, 3 H, NCH$_3$), 1.86 (s, 1 H, CH), 1.02 (s, 3 H, CH$_3$), 0.48 (s, 3 H, CH$_3$); **4a**, δ 4.82 and 2.63 (2d, 2 H, CH$_2$, $^2J_{HA-HB}$ = 11.7 Hz), 3.86 (s, 3 H, CO$_2$CH$_3$), 3.43 (s, 3 H, CO$_2$CH$_3$), 3.0 (s, 3 H, NCH$_3$), 2.82 (s, 3 H, NCH$_3$), 1.22 (s, 3 H, CH$_3$), 0.69 (s, 3 H, CH$_3$). ^{13}C NMR (50.32 MHz, CDCl$_3$, 20 °C); **2a**: 109.4 (C^b), 73.1 (C^a), 67.9 (CH$_2$), 51.6 and 46.2 (NCH$_3$), 26.9 and 22.1 ppm (CH$_3$); **2b**, 69.4 (CH allylic), 68.1 (CH$_2$), 52.5 and 51.6 (NCH$_3$), 46.4 (CO$_2$*C*H$_3$), 24.3 and 22.8 ppm (CH$_3$); **4b**, 65.6 (CH$_2$), 51.7 (2NCH$_3$), 51.1 (CH), 34.7 (CO$_2$*C*H$_3$), 25.4 and 24.7 ppm (CH$_3$).

(12) The assignment of H^a and H^b of the π-allyl ligands follows that found in the related complexes reported in the following references. (a) Hayashi, T.; Hagihara, T.; Konishi, M.; Kumada, H. *J. Am. Chem. Soc.* **1983**, *105*, 7768. (b) Hegedus, L. S.; Åkermark, B.; Olsen, D. J.; Anderson, O. P.; Zetterberg, K. *J. Am. Chem. Soc.* **1982**, *104*, 697–704. (c) Clemens, P. R.; Hughes, R. P.; Margerum, L. D. *J. Am. Chem. Soc.* **1982**, *103*, 2428–2430. (d) Grenouillet, P.; Neibecker, D.; Tkatchenko, I. *Inorg. Chem.* **1980**, *19*, 3189–3191. (e) Sadownick, J. A.; Lippard, S. J. *Inorg. Chem.* **1973**, *12* 2659.

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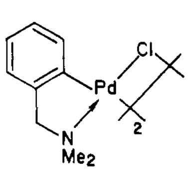
tallization, each as bright yellow crystals. Analytical data show that they have the same empirical formula and that one cyclopropene molecule per palladium atom has again been added to the starting material.



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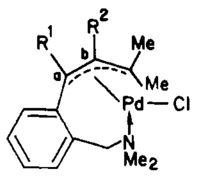
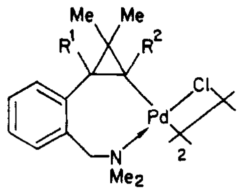
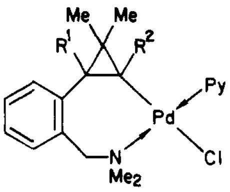


2a, $R^1 = R^2 = H$
b, $R^1 = H$; $R^2 = CO_2Me$



3a, $R^1 = R^2 = CO_2Me$
b, $R^1 = H$; $R^2 = CO_2Me$



4a, $R^1 = R^2 = CO_2Me$
b, $R^1 = H$; $R^2 = CO_2Me$

In compound **2b** the presence of the CO_2Me group is detected in the IR spectrum by an intense absorption at 1720 cm^{-1}. The ^1H and ^{13}C NMR spectra show that only one isomeric form is present and, therefore, that the reaction is regiospecific. Taking into account the substitution of one vinylic proton of the cyclopropene by a CO_2Me moiety, the NMR spectra of **2a** and **2b** are closely related. It is thus very likely that the formation of **2b** has also occurred via the cleavage of a C–C single bond of the cycloalkene. The chemical shift of the vinylic proton (δ 4.78) and that of the corresponding carbon atom (δ 69.4) are very close to those of H^a and C^a in **2a**.[12] We therefore propose that in **2b** the vinylic CH group is adjacent to the phenyl ring of the dmba. Consequently, it is the C–C bond opposite the CO_2Me in the triangular olefin that has been cleaved to give **2b**.

The IR spectrum of **3b** shows two ν(CO) absorptions for the CO_2Me group, at 1692 and 1675 cm^{-1}. In addition, each set of protons in the ^1H NMR spectrum gives rise to a complicated multiplet, suggesting that **3b** consists of a mixture of isomers. However, reaction with pyridine affords compound **4b** as only one isomeric form in which one pyridine is found per Pd atom. These observations are strong evidence that **3b** is a mixture of cis and trans isomers of a chloride-bridged dimer.[14] The ^1H NMR spectrum of **4b** shows again the diastereotopic nature of both the NMe_2 and the CH_2 groups of the dmba. However, the singlet resonance at δ 1.86 obviously can no longer be due to a vinylic proton but is instead assigned to a proton of a cyclopropyl moiety;[4d] thus, the insertion of the olefin into the Pd–C bond of **1** has occurred without any C–C bond cleavage.

The reaction of 1,2-dicarbomethoxy-3,3-dimethylcyclopropene with **1**, on the other hand, affords only one compound, **3a**, which has spectroscopic data and chemical properties close to those of **3b**. It too gives a pyridine adduct, **4a**, when treated with this ligand and it is, therefore, reasonable to infer that **3a** and **3b** have similar structures. In order to ascertain the geometry of these compounds, we have performed an X-ray diffraction study on compound **4b**.[15] An Ortep diagram of its molecular structure is shown in Figure 1. It is at once apparent that the cyclopropene has indeed been inserted into the Pd–C bond of **1**, affording a new seven-membered organometallic ring. The geometry around Pd is that of a slightly distorted square plane; the pyridine is located trans to the nitrogen atom of the dmba moiety, whereas the chloride atom is found trans to C1 of the cyclopropyl ring σ-bonded to Pd. The Pd–C1, Pd–N, and Pd–Cl bond distances are within the expected ranges for these bonds.[9] The geometric features of the C1–C3 triangular unit compare well with those found in a related compound containing palladated cyclopropyl groups.[16] The Pd atom and C4 of the dmba are in cis positions with respect to the plane of the cyclopropyl triangle; since the CO_2Me unit is found at the carbon C1 σ-bonded to Pd, it is the less hindered carbon atom of the ring (i.e., C3) which is close to the phenyl of the dmba, a result that is in accord with what we observed in related reactions of **1** with unsymmetrically substituted alkynes.[9a] The geometry of the new seven-membered organometallic ring compares well with that of related metallocyclic units obtained by the insertioin of hexafluorobut-2-yne into the Pd–C bond of **1**.[9b] It has adopted a boat configuration so that the plane of the phenyl ring of the dmba is almost perpendicular to the coordination plane of the Pd atom.

This study has shown that cyclopropenes can behave like alkynes in that they can insert into metal–carbon σ bonds to afford new organometallic species. Clearly, the presence of electron-withdrawing substituents such as CO_2Me seems to favor the insertion of these strained olefins without C–C bond cleavage, whereas an opposite trend is observed for unsubstituted cyclopropene. Further work to fully understand the role of the substituents and the mechanisms of these reactions is under contemplation.

Acknowledgment. We thank Dr. M. Franck-Neumann for stimulating discussions, Dr. M. Miesch for providing us the CO_2Me-substituted cyclopropenes, Dr. M. Morris for his help in the preparation of the manuscript, and the CNRS for the award of a fellowship (to F.M.).

Registry No. **1**, 18987-59-2; **2a**, 102307-43-7; **2b**, 102307-44-8; **3a**, 102307-45-9; **3b**, 102307-46-0; **4a**, 102307-47-1; **4b**, 102342-01-8; 3,3-dimethylbyclopropene, 3907-06-0; 1-carbomethoxy-3,3-dimethylcyclopropene, 21603-22-5; 1,2-dicarbomethoxy-3,3-dimethylcyclopropene, 21603-23-6.

Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, bond lengths and angles, a selection of least-squares planes, and structure factors for **4b** (26 pages). Ordering information is given on any current masthead page.

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(14) In the case of the unsymmetrically substituted cyclopropene, we have checked that compound **3b** is not an intermediate in the formation of **2b**; heating **3b** in refluxing acetonitrile for 2 days did not lead to any detectable amount of **2b**, **3b** being recovered quantitatively after the reaction.

(15) Crystals are orthorombic with space group $P2_12_12_1$ with a = 12.408 (5) Å, b = 16.315 (4) Å, c = 10.423 (5) Å, and V = 2109.9 Å^3: ρ_{calcd} (Z = 4) = 1.51 g cm^{-3}. X-ray data diffraction intensities were collected on an Enraf-Nonius CAD-4 automatic diffractometer employing graphite-monochromatized Mo Kα radiation [$\lambda(\bar{\alpha})$ = 0.710 73 Å]. No absorption correction (μ = 10.1 cm^{-1}) was applied. Of a total of 2904 reflections with θ <28°, 2579 were observed [$I > \sigma(I)$]. The calculations were performed as described in a previous paper in this series.[1] The structure was solved by MULTAN and subsequent Fourier-difference synthesis for the 27 independent non-hydrogen atoms. After refinement of coordinates and thermal parameters, first isotropic and then anisotropic, of these atoms, the positions of the 27 hydrogen atoms were calculated and located for most of them, on a Fourier difference synthesis. Introduction of these hydrogen atoms into the refinement, with coordinates and isotropic thermal parameters of 5 Å^2 held fixed, was significant. Final values of R = 0.028 and R_ω = 0.038 were obtained after two last cycles of refinement of non-hydrogen atoms.

(16) Büch, H. M.; Krüger, C. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1984**, *C40*, 28.