Upon additon of ^{13}CO the 2189-cm^{-1} absorption shifts to 2140 cm^{-1}. No intermediate absorptions are observed when $\sim$50% ^{12}CO and $\sim$50% ^{13}CO are added. The strong similarity between the 468- and 520-cm^{-1} transitions suggests that the 468-cm^{-1} absorption is due to a Cl–Ni–Cl asymmetric stretch of an $NiCl_2CO$ complex. Addition of N_2 to the argon results in a new absorption at 483 cm^{-1}. This is assigned to an $NiCl_2N_2$ complex. Both of these transitions can be fit very well using the isotope relation for free $NiCl_2$ assuming a 180° Cl–Ni–Cl bond angle.

The frequency of the C–O stretch in these complexes is of interest since to our knowledge no other metal carbonyls exhibit stretching frequencies as high as observed here. It is well known that the C–O frequency increases upon metal–carbon σ-bond formation while M–CO π bonding reduces the C–O frequency.[4] We suggest that the NiX_2CO complexes may best be thought of as entirely σ-bonded systems.[5]

Less can be said about the nitrogen complex since the N–N stretch is unobserved. The nickel and chlorine isotopic structure for NiF_2 and $NiCl_2$ again supports little or no change in the X–Ni–X bond angle upon complex formation. In fact, Margrave, et al.,[1e] found that the 483-cm^{-1} absorption for $NiCl_2$ could be fit very well assuming a 180° angle for $NiCl_2$. They, however, interpreted the 483-cm^{-1} absorption as $NiCl_2$ present in a different site. Although it is difficult to argue that this is not the case, yet it would appear from the definite NiX_2CO complex formation that a weakly bound nitrogen complex is forming.

(4) L. H. Jones, *J. Mol. Spectrosc.*, 9, 130 (1962).
(5) See, for example, the discussion on σ-bonded complexes in T. C. Brown and D. J. Darensbourg, *Inorg. Chem.*, 6, 971 (1967).

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Structure of $C_5Me_5CH(p\text{-tolyl})CH_2Pd(acac)$, a σ,π-Organopalladium Complex, from the Trimerization of 2-Butyne with Tolylpalladium Chloride. A *Dihapto*cyclopentadiene

Sir:

We recently described the reaction of 2-butyne with $PdCl_2$ to give a complex $[Cl(C_2Me_2)_3PdCl]_2$ (**1a**).[1] In our analysis of the reaction we suggested that it proceeded by initial coordination of one molecule of 2-butyne to $PdCl_2$ (**ia**) followed by a relatively slow (rate-determining) cis insertion of the acetylene into a Pd–Cl bond to give a σ-vinyl intermediate **iia**. This can then react by a series of fast cis-insertion reactions (*via* **iiia**) with more butyne to build up a helical chain until the reaction stops (for steric reasons), largely at **1a**.

(1) (a) H. Dietl, H. Reinheimer, J. Moffat, and P. M. Maitlis, *J. Amer. Chem. Soc.*, 92, 2276 (1970); (b) H. Reinheimer, J. Moffat, and P. M. Maitlis, *ibid.*, 92, 2285 (1970); (c) P. M. Maitlis, "The Organic Chemistry of Palladium," Vol. II, Academic Press, New York, N. Y., 1971, pp 51-57.


a, X = Cl; b, X = Ph

R = Me
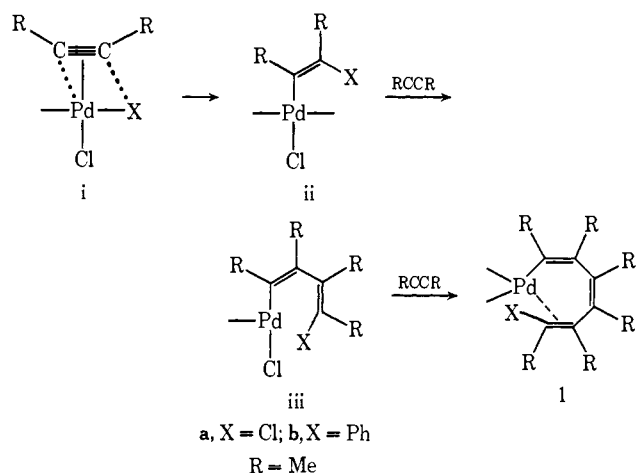
If this proposal is correct then it should be even easier to carry out this reaction with "phenylpalladium chloride"[2] since insertion generally occurs more easily into a Pd–C than into a Pd–Cl bond. We have treated 2-butyne with diphenylmercury and bis(benzonitrile)-palladium chloride (molar ratio 7:1:1) in either benzene or dichloromethane at 20° and have obtained in 45% yield a crystalline complex **2**,[4] stoichiometrically analogous to **1a** (Ph in place of one Cl), but with a totally different type of ^1H nmr spectrum. In CDCl$_3$ and other noncoordinating solvents the spectrum is very complex owing to an exchange process; this, however, does not occur in CDCl$_3$–DMSO-d_6 (1:2) where clearly resolved resonances at δ 0.82 (s, 3 H), 1.48 (s, 3 H), 1.82 (s, 6 H), 1.91 (s, 3 H) 2.15 (bd m, *ca.* 2 H), 2.40 (bd m, *ca.* 1 H), and 7.28 and 7.96 (bd m, 5 H, aromatic) are observed. The complex **2** can be recovered unchanged from the solution.

On the basis of this spectrum, the analysis, and molecular weight, we proposed the structure shown for **2**; we further suggest that it arises by the reaction sequence indicated from **1b** (formed *via* **ib**, **iib**, and **iiib**) in which cyclization first occurs to give **iv**. Models show that a σ,π-bonded structure is highly strained for **iv** and it is not surprising that it undergoes a 1,2-hydride shift to give **2**.
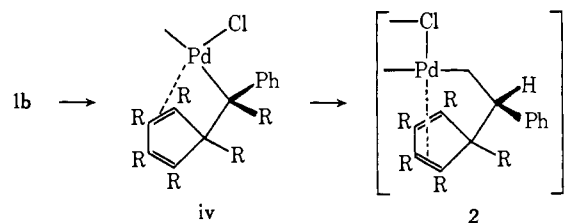
In order to confirm the proposed structure we have carried out an X-ray determination. Unfortunately, crystals of **2** were not suitable for X-ray analysis, but the closely related acetylacetonate

$$C_5Me_5CH(p\text{-tolyl})CH_2Pd(acac)$$

3
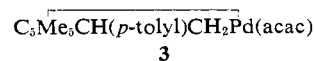
(2) A phenylpalladium species, which we have arbitrarily designated as "PhPdCl," is formed *in situ* from reaction of $PdCl_2$ and Ph_2Hg.[3]
(3) R. F. Heck, *J. Amer. Chem. Soc.*, 90, 5518 (1968), and following papers.
(4) No **1a** and only a trace of hexamethylbenzene were formed in this reaction; however, a tetrameric complex of empirical formula $[Ph(C_2Me_2)_4PdCl]_2$ was also isolated in 4% yield.
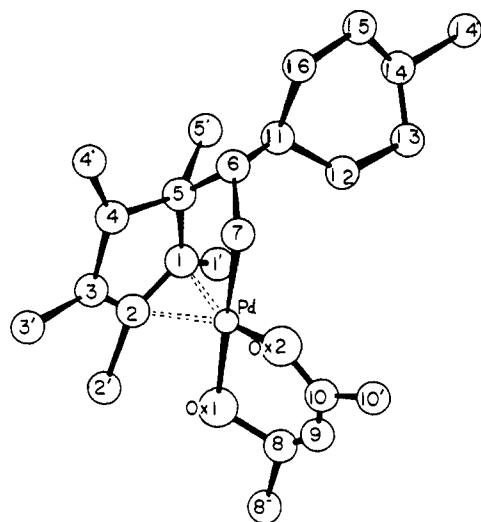
Figure 1. The structure of C₅Me₅CH(p-tolyl)CH₂Pd(acac) (3); all the numbered atoms are carbons and all hydrogen atoms are omitted.

derived from "p-tolylpalladium chloride" gave good crystals.[5]

The complex crystallized in the triclinic system with space group $P\bar{1}$ and lattice parameters $a = 11.072$ (5), $b = 10.034$ (5), $c = 13.515$ (5) Å; $\alpha = 119.21$ (5), $\beta = 88.23$ (5), and $\gamma = 63.90$ (5)°. The unit cell contained two molecules [$\rho_{obsd} = 1.36$ (by flotation), $\rho_{calcd} = 1.353$ g/cm³] of two optical enantiomers; one is depicted, the other is related to it by a center of symmetry.

The structure was solved from Patterson and electron density maps using 1147 observed reflections out of 1316 measured with Mo Kα radiation on a Syntex automatic diffractometer. It was refined to a conventional R value of 0.055 and a weighted R of 0.078. The molecular geometry is shown (Figure 1) and the most significant bond lengths are given in Table I. The

Table I

Bond lengths, Å		Bond angles,[a] deg	
Pd–Ox(1)	2.048 (11)	Ox(1)–Pd–C(7)	85
Pd–Ox(2)	2.158 (9)	Ox(1)–Pd–Ox(2)	89
Pd–C(1)	2.130 (16)	Ox(2)–Pd–C(7)	172
Pd–C(2)	2.296 (17)	Pd–C(7)–C(6)	109
Pd–C(3)	3.14 (2)	C(7)–C(6)–C(5)	108
Pd–C(4)	3.48 (2)	C(7)–C(6)–C(11)	114
Pd–C(5)	3.04 (2)	C(5)–C(6)–C(11)	113
Pd–C(7)	2.025 (12)	C(6)–C(5)–C(5')	115
C(1)–C(2)	1.39 (2)	C(6)–C(5)–C(1)	108
C(2)–C(3)	1.47 (3)	C(6)–C(5)–C(4)	107
C(3)–C(4)	1.31 (2)	C(5)–C(1)–C(2)	109
C(4)–C(5)	1.54 (3)	C(1)–C(2)–C(3)	109
C(5)–C(1)	1.55 (2)	C(2)–C(3)–C(4)	110
C(5)–C(6)	1.56 (2)	C(3)–C(4)–C(5)	112
C(6)–C(7)	1.54 (2)	C(4)–C(5)–C(1)	100

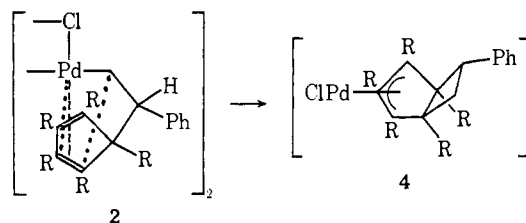[a] Esd's are about 1.0°.

geometry of 3 is very unusual and consists of a cyclopentadiene which has only *one* double bond [C(1)–C(2)]

coordinated to the metal, and which is σ bonded to the metal *via* a –CH(p-tolyl)CH₂– bridge from C(5). As expected, the coordinated double bond is longer [C(1)–C(2) 1.39 (2) Å] than the uncoordinated one [C(3)–C(4) 1.31 (2) Å], and the coordination plane of the metal is approximately perpendicular (88°) to C(1)–C(2). The two remaining coordination sites of the square-planar palladium are occupied by the acetylacetonate. The isomers present in the crystal have the p-tolyl group and the *coordinated* double bond on the same side (taking the cyclopentadiene plane as horizontal). Bond angles and bond lengths are mostly very normal, in particular the angles Pd–C(7)–C(6) and C(7)–C(6)–C(5) are tetrahedral and therefore show that there is no strain present in the five-membered chelate ring (compare formula iv, above). The Pd–C σ bond [2.025 (16) Å] exerts a large influence on the Pd–O bond trans to itself [Pd–Ox(1) = 2.158 (9) Å, Pd–Ox(2) = 2.048 (11) Å].[6]

Furthermore, models of 2 and 3 show that another strain-free conformer can exist which has the coordinated double bond nearly coplanar with the coordination plane of the metal. These molecules are therefore well aranged geometrically for a variety of insertion and other reactions. For example, 2 isomerizes on standing in solution slowly to 4;[8] others are described in the following communication.[9]

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A Model System for Acid and Base Reactions, Carbonylation, and β-Hydride Elimination in Organopalladium Chemistry

Sir:

Alkylpalladium(II) complexes have been widely suggested as intermediates in a large number of catalytic reactions.[1] However, there has been relatively little evidence from model systems containing alkyl–Pd bonds to substantiate these mechanistic suggestions. This is largely because many of the alkylpalladium complexes

(1) P. M. Maitlis, "The Organic Chemistry of Palladium," Vol. II, Academic Press, New York, N. Y., 1971, and references therein.