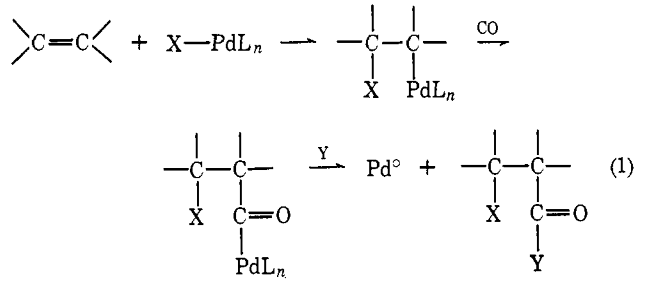
Stereochemistry of Carbonylation of Palladium–Bicyclo[2.2.1]heptadiene Complexes

Sir:

The palladium-catalyzed carbonylation of olefins affords β-chloroacyl chlorides when benzene is the reaction solvent while saturated esters are obtained in alcohols.[1] In these reactions, palladium–carbon σ-bonded complexes resulting from the addition of X–Pd to the olefin have been postulated as intermediates which subsequently undergo an intramolecular rearrangement to acyl complexes; the acyl complexes decompose to afford the observed products (eq 1).



(1)

benzene, X = Y = Cl
ROH, X = H, Y = OR

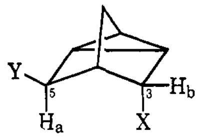
The oxymetallation reaction of platinum- and palladium–diolefin complexes in alcohol takes place with overall *trans* addition of the alkoxy and metal addends across the double bond to afford stable platinum or palladium σ- or π-allyl bonded complexes.[2,3] Dichloro(norbornadiene)palladium (I) undergoes nucleophilic attack by methanol to afford an adduct which is probably best formulated as a π-homoallylic system IIb (instead of the σ-complex IIa) in which the methoxy group is *exo* and the palladium *endo*.[3,4]

Although the mechanisms of the carbonylation reactions have been studied, little information concerning the stereochemistry of insertion of carbon monoxide into the carbon–metal bond is available. We report here results obtained from a study of the carbonylation of the complexes, I and II.

Passing carbon monoxide through a suspension of II in methanol at room temperature resulted in the precipitation of palladium metal and a soluble, single product, 3-*endo*-carbomethoxy-5-*exo*-methoxynortricyclene (IIIa).[5] Similarly, carbonylation of the diolefin complex, I, in methanol or ethanol produced IIIa and IIIb, respectively.

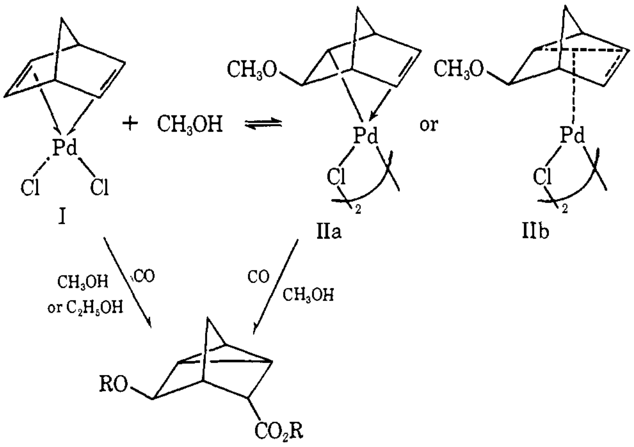
The geometry at the 3 and 5 positions in IIIa and IIIb was determined by nmr chemical shifts. It has been shown[6] that *exo* substituents at the 3 position have little or no effect on the chemical shift of an *exo* or *endo* 5 proton, while an *endo*-3 substituent produces a paramagnetic shift in a 5-*endo* proton. The nmr data contained in Table I reveal that the proton on the 5 carbon (H_a) in IIIa and IIIb has experienced a downfield shift relative to the corresponding proton in the parent ether ($\delta_{H_a} = \sim 3.4$, X = H). The proton on the 3 carbon (H_b) in IIIa and IIIb has essentially the same chemical shift found for H_b in the parent esters (δ_{H_b} = 2.5, Y = H). Treatment of IIIa with sodium methoxide produced a mixture of IIIa and its epimer. The nmr spectrum of the epimer was in good agreement with that expected for 3-*exo*-carbomethoxy-5-*exo*-methoxynortricyclene (δ_{H_a} = 3.39). The proton on the carbon bearing the methyl ester group experienced almost no change in chemical shift (δ_{H_b} = 2.46).

Table I. Chemical Shift Data for Substituted Nortricyclenes[a]



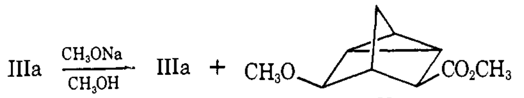
	Structure	δ, ppm H_a	δ, ppm H_b
	X = H; Y = OCH_3	3.39	1.15
IIIa	(X = CO_2CH_3; Y = OCH_3)	3.75	2.52
IIIb	(X = $CO_2C_2H_5$; Y = OC_2H_5)	3.80	2.48
V	(X = $CO_2C_2H_5$; Y = OCH_3)	3.70	2.48
VI	(X = CO_2CH_3; Y = Cl)	4.23	2.58
	X = H; Y = Cl	3.87	~1.2–1.3

[a] 60 MHz; $CDCl_3$.



I IIa IIb

IIIa, R = CH_3
b, R = C_2H_5



IV

The carbonylation of dichloro(1,5-cyclooctadiene)palladium in ethanol has been reported[7] to produce a mixture of an unsaturated mono- and a saturated diester. The difference in behavior is possibly a result of the relative abilities of the two complexes to undergo an oxypalladation reaction in the presence of the hydrogen chloride produced in the carbonylation reaction.[8] We have found that only a minor amount of II is converted into the diolefin complex I by

---

(1) J. Tsuji, *Accounts Chem. Res.*, 2, 144 (1969).

(2) J. Chatt, L. M. Vallarino, and L. M. Venanzi, *J. Chem. Soc.*, 2496 (1957); J. Chatt, L. M. Vallarino, and L. M. Venanzi, *ibid.*, 3413 (1957).

(3) J. K. Stille, R. A. Morgan, D. D. Whitehurst, and J. R. Doyle, *J. Amer. Chem. Soc.*, 87, 3282 (1965); J. K. Stille and R. A. Morgan, *ibid.*, 88, 5135 (1966).

(4) M. Green and R. I. Hancock, *J. Chem. Soc.*, *A*, 2054 (1967).

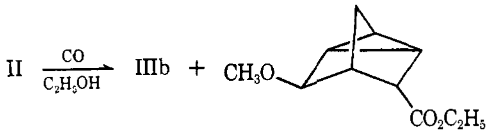
(5) Satisfactory analytical data were obtained for all new products. The infrared spectra (neat) of all carbonylation products contained, in addition to strong ether and ester absorptions, a band at ~810–815 cm^{-1} characteristic of the nortricyclene ring system.[6]

(6) D. R. Coulson, *J. Amer. Chem. Soc.*, 91, 200 (1969).

(7) J. Tsuji, S. Hosaka, T. Suzuki, and J. Kiji, *Bull. Chem. Soc. Jap.*, 39, 141 (1966).

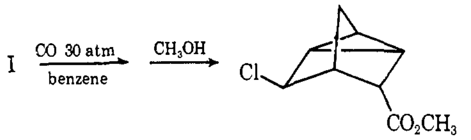
(8) The presence of a base such as alkoxide ion, sodium acetate, or sodium carbonate is needed to prepare the alkoxy addition products of dichloro(norbornadiene)palladium and dichloro(1,5-cyclooctadiene)palladium. Removal of the hydrogen chloride by the base shifts the equilibrium in favor of the oxymetallation product. Surprisingly we

reaction with the hydrogen chloride liberated during the carbonylation. When II was carbonylated in ethanol a mixture of IIIb (7%) and 3-*endo*-carboethoxy-5-*exo*-methoxynortricyclene, V (93%), was obtained.[9]



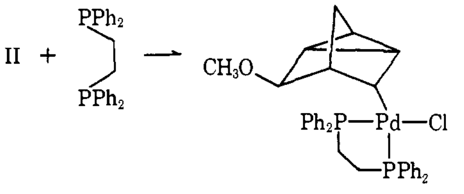
V

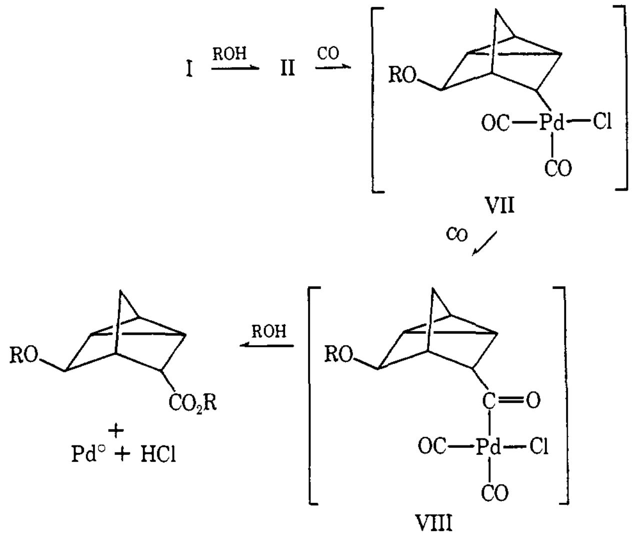
Carbonylation of I in benzene gave a product resulting from an initial *trans* addition of Cl–Pd to the coordinated double bond. The acid chloride which was obtained was converted to the methyl ester, 3-*endo*-carbomethoxy-5-*exo*-chloronortricyclene (VI).



VI

These results are in general agreement with the proposed mechanism (eq 1). Reaction of II with carbon monoxide forms the σ-bonded complex VII[10] which undergoes an alkyl–acyl rearrangement *with retention* to VIII.





VII

VIII

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

---

have found that II can be carbonylated in methanol to give IIIa even when the solution is saturated with dry hydrogen chloride.

[9] The total conversion of II to IIIb and V was ~90%. The stereochemistry of V is based on nmr data.

[10] Formulation of the alkyl intermediate VII as shown is reasonable if analogy is made to the bridge cleavage reaction of II by 1,2-bis(diphenylphosphino)ethane which produces a stable complex containing the nortricyclene ring system.[6]

John K. Stille, Leon F. Hines
Department of Chemistry, University of Iowa
Iowa City, Iowa 52240

Received January 9, 1970

Gadolinium Sesquichloride, an Unusual Example of Metal–Metal Bonding[1]

Sir:

Among the results of numerous studies[2,3] of rare earth metal–metal halide systems carried out in this laboratory, perhaps the most unexpected was the discovery of a lower gadolinium chloride.[4] The composition of the compound was concluded to be $GdCl_{1.58 \pm 0.06}$, with the range based on estimated upper and lower limits for the amount of $GdCl_3$ impurity which could have been detected in powder patterns of different compositions. Subsequent magnetic measurements[5] found only the paramagnetism of the $4f^7$ metal cores with evidence for an antiferromagnetic ordering near 50°K.

Crystals of the reduced phase produced as before[4] continued to be inadequate for a structural investigation. However, reaction of $GdCl_3$ vapor with the metal at 610° for several days did produce large single crystals. These could not be cut further without the characteristic "fraying,"[4] so data were taken on a relatively large pentagonal prism 70 × 480 μ. The monoclinic cell dimensions are $a = 15.237 \pm 0.004$, $b = 3.896 \pm 0.001$, $c = 10.179 \pm 0.003$ Å, $\beta = 117.66 \pm 0.03°$, and extinctions for only $(h + k)$ odd indicate space groups C2/m, C2, or Cm. A density of 5.14 ± 0.3 g cm^{-3} determined micropycnometrically using $CHCl_3$ compares with 5.23 g cm^{-3} calculated for the final structure Gd_8Cl_{12}. A total of 1378 integrated intensities (1331 observed above the $3\sigma_F$ level) were measured with Mo Kα radiation in two independent octants using an automated, four-circle diffractometer.[6] The raw data were corrected for the usual effects, including absorption using Busing and Levy's[7] method for a general polyhedron. The Patterson map was successfully interpreted in the acentric space group Cm for the positions of four independent metal atoms, while the six chlorine atoms were located by Fourier synthesis maps. Full-matrix least-squares refinement with atomic scattering factors corrected for anomalous dispersion and using all data, unit weights, and isotropic temperature factors gave $R = 0.073$, while the use of anisotropic thermal parameters yielded $R = 0.052$. Atom positions and the isotropic temperature factors are given in Table I. Standard deviations in distances between neighboring metals were ±0.004 Å or less (including the uncertainty in the unit cell dimensions) while those in distances to chlorine were ≤ 0.02 Å. The final difference map was smooth to better than 1.5 e/Å^3, thereby also confirming unit occupancy of sites. Electron microprobe and emission spectroscopic examinations of single crystals also established the absence of foreign metals, and the 100

---

[1] Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 2685.

[2] J. D. Corbett, R. A. Sallach, and D. A. Lokken, Advances in Chemistry Series, No. 71, American Chemical Society, Washington, D. C., 1967, p 56.

[3] P. E. Caro and J. D. Corbett, *J. Less-Common Metals*, **18**, 1 (1969).

[4] J. E. Mee and J. D. Corbett, *Inorg. Chem.*, **4**, 88 (1965).

[5] J. D. Greiner, J. F. Smith, J. D. Corbett, and F. J. Jelinek, *J. Inorg. Nucl. Chem.*, **28**, 971 (1966).

[6] D. J. Dahm, J. E. Benson, D. M. Nimrod, D. R. Fitzwater, and R. A. Jacobson, USAEC Report IS-1052, Ames Laboratory, Iowa State University, 1967.

[7] W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **10**, 180 (1957).