of reactions of coordinated ligands for the production of new ligand systems with a high degree of stereoselectivity. This selectivity is a result of conformational and substituent orientation effects of the chelate rings.

So far as I am aware this is the only example of a macrocyclic ligand that incorporates a piperidine ring. A recent review lists literally dozens of macrocyclic compounds that contain pyridine moieties as subunits.[14] Many of these compounds were developed as metal-complexing agents. A large number of new ligands could be prepared by reduction of the pyridine subunits. If these reductions can be performed on the metal complexes, a higher degree of stereoselectivity may be expected.

Experimental Section

Complexes **1** and **2** were prepared according to the literature procedures.[2]

Raney-Nickel-Catalyzed Reductions. Reductions were done on ca. 2.5 g of **1** or **2** in 200 mL of water. Two to five grams of Raney nickel (W-2 or Grace Grade 28) was added and the mixture placed under 50 psi H_2 (Parr apparatus) and agitated until gas uptake ceased (3–5 h). After removal of the catalyst, solutions were acidified with a few drops of concentrated $HClO_4$ and evaporated to small volumes (~10 mL). The yellow-orange products that crystallized were collected and dried in vacuo. Yields were in the range 60–85%. Recrystallization of the product from **1** or **2** from acidified ethanol–water mixtures gave yellow and/or orange crystals. In one instance, orange crystals grew initially but slowly disappeared to be replaced by yellow. The yellow form could be separated from the orange by preferential dissolution of the latter in acetone. Crystallization of either form from acetone by addition of ether gave only the orange material. Anal. Calcd for $NiC_{15}H_{32}N_4Cl_2O_8$: C, 34.25; H, 6.13; N, 10.65. Found (yellow form): C, 34.27; H, 6.12; N, 10.94. Found (orange form): C, 34.31; H, 6.11; N, 10.93.

Visible spectra of **4** were determined on 10^{-3} M solutions in 5-cm cells with the use of a Cary 14 spectrophotometer or 1-cm cells with the use of a Beckman Acta V. NMR spectra were obtained at 100 and 220 MHz on trifluoroacetic acid solutions. The oxidation potential of **4** was determined by cyclic voltammetry using a standard three-electrode cell and a spherical platinum working electrode. Measurements were made on 10^{-3} M CH_3CN/0.1 M n-Bu_4NBF_4 solutions and potentials measured relative to a 0.1 M Ag^+/Ag reference electrode. At a 200 mV/s scan rate the peak current ratio was unity and the peak separation was 80 mV.

Registry No. **1**, 35270-39-4; **2**, 26149-43-9; **4**, 74185-30-1.

(14) Newkome, G. R.; Sauer, J. D.; Roper, J. M.; Hager, D. C. *Chem. Rev.* **1977**, *77*, 513–597.

Contribution from the Institut de Recherches sur la Catalyse, 69626 Villeurbanne Cédex, France

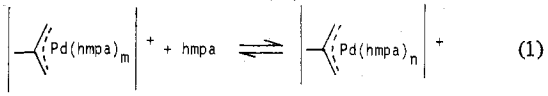
Cationic η^3-Allyl Complexes. 6. New General Synthesis of Cationic (η^3-Allyl)palladium Complexes

Pierre Grenouillet, Denis Neibecker, and Igor Tkatchenko*

Received March 27, 1980

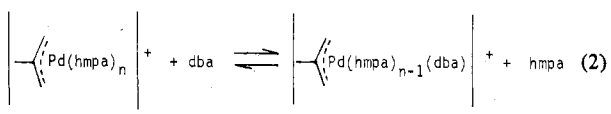
D.N.[1,2] has recently reported that (allyloxy)phosphonium (**1**) and (allylthio)uronium (**2**) salts react readily with zerovalent nickel compounds like nickel carbonyl and bis(1,5-cyclooctadiene)nickel to lead to cationic allylnickel complexes. The corresponding palladium complexes $[Pd(all)L_2]^+$ have been already reported for L = R_3P, R_3As, and coordinating solvents and L_2 = dienes, hexamethylbenzene, etc....[3] These syntheses generally require the use of silver[3b,d,e] and thallium salts[3c] of so-called noncomplexing anions or sodium tetraphenylborate.[3a] We report here an extension of the general procedure used for nickel which uses easily accessible zerovalent palladium compounds, i.e., tris(dibenzylideneacetone)dipalladium, $Pd_2(dba)_3$ (**3**),[4] or bis(dibenzylideneacetone)palladium (**4**),[5] and allylic salts[6,7] together with preliminary observations on the mechanism of the formation of these complexes.

As stated by Ishii and his co-workers,[8] $Pd_2(dba)_3$ reacts smoothly with allyl halides to give allylchloropalladium(II) complexes. Reaction of equimolar amounts of **1a** with **3** in dichloromethane was monitored by UV–vis spectroscopy (10^{-4} M solution). After 2 h, the absorption at 524 nm we assigned to coordinated dba vanished and a stable, yellow solution containing free dba was obtained. ^1H NMR spectroscopy (CH_2Cl_2, 10^{-1} M) shows the presence of a 2-methallyl ligand (δ 2.29, s, 2-methyl; δ 2.98, s, anti H; δ 3.93, s, syn H, assuming the resonance of CH_2Cl_2 at 5.35 ppm) together with the signals awaited for hexamethylphosphorotriamide, hmpa (δ = 2.66, ^3J(H–P) = 9.5 Hz) and dibenzylideneacetone (δ = 7–8). Proton-decoupled ^{31}P NMR spectroscopy indicates the coordination of hmpa to the Pd(II) ion (δ = +36 for the salt **1a**, δ = +30.4 for the solution of complex **5**, δ = 24.1 for free hmpa, in CH_2Cl_2). Addition of increments of hmpa indicate a monotonic shift of the ^{31}P signals toward the position observed for a solution of hmpa in CH_2Cl_2 (i.e., 1 equiv of hmpa, δ = 29.4; 3 equiv of hmpa, δ = 27.0; 9 equiv of hmpa, δ = 25.2), suggesting the occurrence of the exchange



(1)

Futhermore, the syn and anti protons of the 2-methylallyl ligand are also affected by the addition of hmpa. Thus, addition of 1 equiv of hmpa shifts the H_{syn} and H_{anti} signals to 3.67 and 2.67 ppm. Noteworthy is that complex **6a** (vide infra) shows H_{syn} and H_{anti} resonances at 3.87 and 2.98 ppm and a ^{31}P resonance at 30.0 ppm, values which are not very different from those observed in the reaction medium containing the evolved dba. Addition of 1 equiv of hmpa to this complex also affects these signals (respectively δ = 3.63 and 2.67). Finally, addition of free dba shifts the position of the same signals, but addition of more than 1 equiv does not further modify their positions (respectively 3.83 and 2.86 ppm). Interestingly, in this case, the vinyl protons of dba are simultaneously *deshielded* by 0.2 ppm with respect to the free ligand and by 1.15 and 2.35 ppm with respect to the coordinated ligands of $Pd_2(dba)_3$.[9] This behavior could be interpreted by the coordination to Pd(II) of the oxygen atom of the carbonyl ligand. Thus another exchange

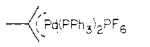
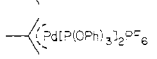
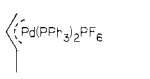
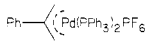
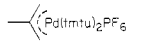
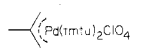
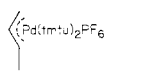
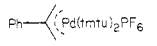


(2)

(1) Neibecker, D.; Castro, B. *J. Organomet. Chem.* **1977**, *134*, 105.
(2) Neibecker, D.; Castro, B. *Tetrahedron Lett.* **1977**, 2351.
(3) (a) Powell, P.; Shaw, B. L. *J. Chem. Soc A* **1968**, 774. (b) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 3089. (c) Johnson, B. F. G.; Lewis, J.; White, D. A. *Synth. Inorg. Met.-Org. Chem.* **1971**, *1*, 235; *Chem. Abstr.* **1972**, *76*, 127149e. (d) Takahashi, Y.; Shizuyoshi, S.; Ishii, Y. *Inorg. Chem.* **1972**, *11*, 1516. (e) Mabbott, D. J.; Mann, B. E.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1977**, 294.
(4) Takahashi, Y.; Ito, T. S.; Sakai, S.; Ishii, Y.; Bonnet, J. J.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *65*, 253.
(5) Rettig, M. F.; Maitlis, P. M. *Inorg. Synth.* **1977**, *17*, 135.
(6) Castro, B.; Selve C. *Bull. Soc. Chim. Fr.* **1971**, 4308 and ref 1.
(7) Neibecker, D.; Castro, B., submitted for publication in *Inorg. Chem.*
(8) Ito, T. S.; Hasegawa, S.; Takahashi, Y.; Ishii, Y. *J. Organomet. Chem.* **1974**, *73*, 401.
(9) Kawazura, H.; Tanaka, H.; Yamada, K.; Takahashi, T.; Ishii, Y. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3466.

0020-1669/80/1319-3189$01.00/0

Table I

no.	complex	procedure (solvent)	yield,[a] %	color	mp, °C	^{1}H NMR[b]
6a		I (CH_2Cl_2)	95			2.24 (s, 3 H, 2-Me), 2.69 (d, ^3J(H-P) = 9.5 Hz, 27 H, NMe), 2.98 (s, 2 H, anti H), 3.87 (s, 2 H, syn H)[e]
6b		I (MeCN) I (CH_2Cl_2) II	92 44	white	230 dec	1.99 (s, 3 H, 2-Me), 3.41 (br, m, 2 H, anti H), 3.75 (br, s, 2 H, syn H)[c]
6c		I (MeCN)	93	white	182 dec	1.96 (s, 3 H, 2-Me), 3.04 (br, m, 2 H, anti H), 4.30 (br, s, 2 H, syn H)[d]
6d		I (CH_2Cl_2)	98	white	182 dec	0.92 (s, 3 H, 2-Me), 2.27 (t, ^3J(H-P) = 9 Hz, 2 H, anti H), 4.0 (t, ^3J(H-P) = 4 Hz, 2 H, syn H)[c]
7a		I (CH_2Cl_2)	85	white	188 dec	*f*
7b		I (CH_2Cl_2)	68	white	146 dec	3.84 (br, m, 2 H, anti H), 4.02 (br, s, 2 H, syn H)[d]
8a		I (CH_2Cl_2) I (MeCN) II	80 89 89	yellow	146 dec	2.05 (s, 3 H, 2-Me), 2.90 (s, 2 H, anti H), 3.26 (s, 24 H, NMe),[c] 3.75 (s, 2 H, syn H)
8b		I (CH_2Cl_2)	100	yellow	145 dec	2.04 (s, 3 H, 2-Me), 2.91 (s, 2 H, anti H), 3.27 (s, 24 H, NMe), 3.77 (s, 2 H, syn H)[d]
8c		I (CH_2Cl_2)	87	yellow	108 dec	*f*
8d		I (CH_2Cl_2)	90	yellow	127 dec	3.12 (s, 26 H, anti H + NMe), 4.08 (s, 2 H, syn H)[d]

[a] The yields were optimized in only some instances. [b] δ relative to Me_4Si with the assumption that δ(CH_2Cl_2) = 5.35 and δ($CHCl_3$) = 7.27 downfield to Me_4Si; s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. [c] In CD_2Cl_2. [d] In $CDCl_3$. [e] In CH_2Cl_2. [f] Room-temperature ^{1}H NMR spectra of poor quality for the 1-methylallyl groups.

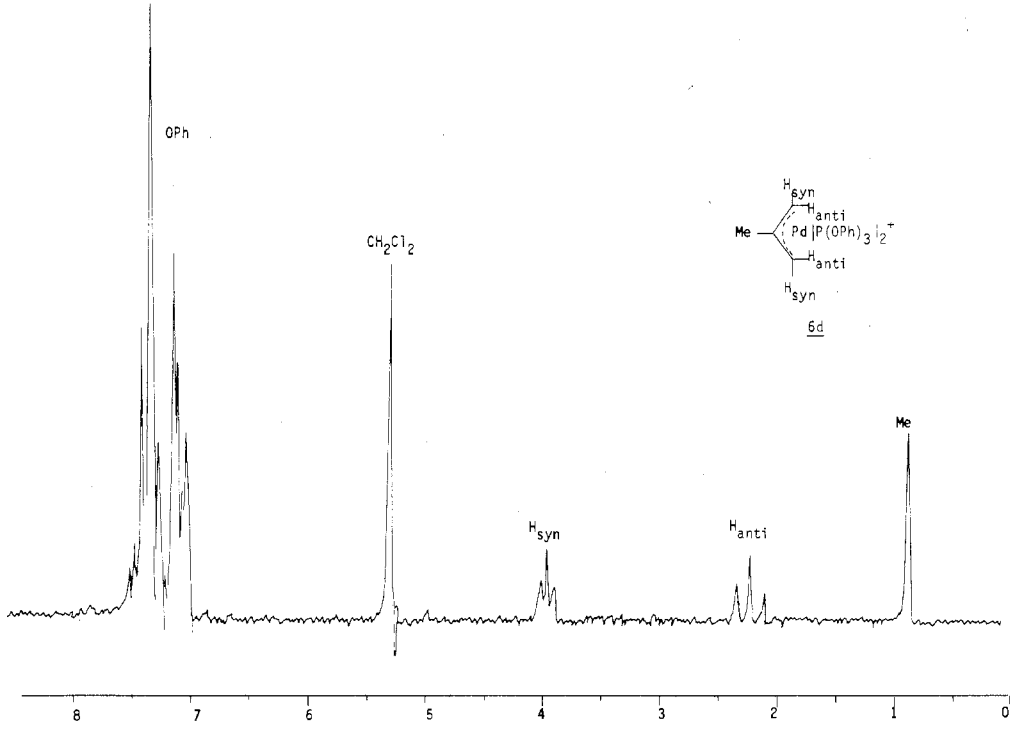


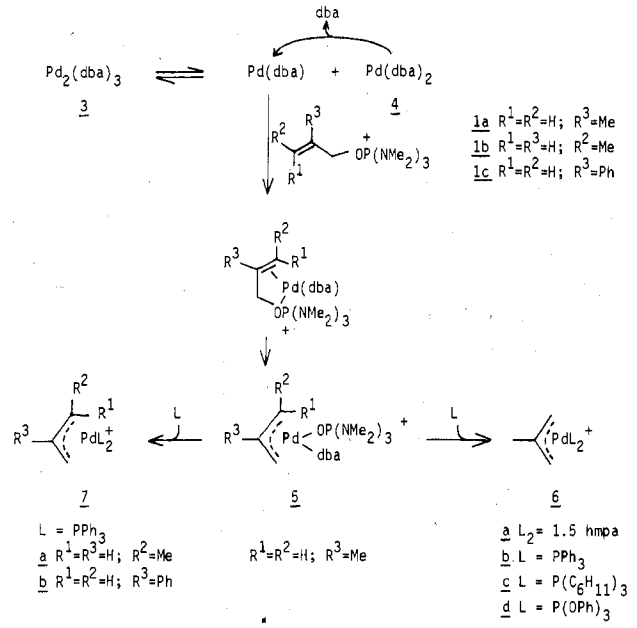
Figure 1. ^{1}H NMR spectrum of complex **6d** in CD_2Cl_2.

is occurring together with (1).

Addition of L ligands to this solution allows for the isolation, after subsequent workup (see Experimental Section), of complexes **6a–d**. Similar complexes (**7**) could be obtained when other (allyloxy)phosphonium salts (**1b–c**) are used. Satisfactory elemental analyses are obtained for these compounds and Table I reports the pertinent spectroscopy data. Noteworthy is that complex **6a** from both microanalysis (Anal. Calcd for $C_{13}H_{34}F_6N_{4.5}O_{1.5}P_{2.5}Pd$: C, 27.14; H, 5.95; N, 10.96; Pd, 18.49. Found: C, 26.94; H, 5.97; N, 10.75; Pd, 18.64) and NMR integration for the dimethylamino groups appears to contain 1.5 equiv of hmpa per allylpalladium cation unit. We are looking for the isolation of suitable crystals for an X-ray investigation in order to determine whether or not the complex is a 14-electron one with hmpa in the lattice.

By comparison with the recent report of Yamamoto and his

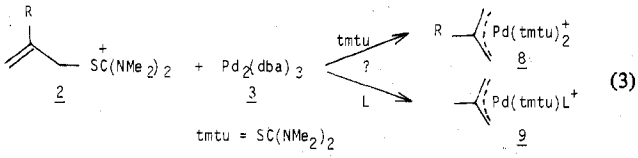
Scheme I



co-workers[10] on the oxidative addition of allyl phenyl ether on nickel(0) compounds, we suggest that the reaction occurs according to Scheme I. Attempts to isolate the intermediate **5** from the reaction mixture have until now failed. Relevant experiments in progress are designed to demonstrate the plausibility of this reaction scheme.

Inspection of Table I shows the expected NMR patterns. However, complex **6d** presents in its ^1H NMR spectrum (Figure 1) an upfield shift of the 2-methyl substituent. This shift could be induced by the shielding of the methyl group through either phenyl group(s) of the phosphite ligands or the interaction of the methyl hydrogens with electron-poor palladium cation via an axial coordination as already reported for other palladium complexes[11] or allyliron complexes.[12] Variable-temperature NMR and X-ray crystallographic studies of this compound will be undertaken in order to assign the origin of this shift.

A similar reaction occurs with the (allylthio)uronium salts **2** leading to complexes **8** and, possibly, mixed-ligand complexes **9** although this opportunity has not yet been investigated.



(3)

Finally, it should be pointed out that the preparation of cationic complexes according to the procedure of Powell and Shaw[3a] could be modified and extended to noncomplexing anions other than tetraphenylborate, like ammonium hexafluorophosphate or lithium perchlorate.

Experimental Section

Procedure I: (η^3-2-Methylallyl)bis(triphenylphosphine)palladium(II) Hexafluorophosphate. In a 50-mL Schlenk tube were successively placed $Pd_2(dba)_3 \cdot CHCl_3$[4] (259 mg, 0.25 mM) and ((2-methylallyl)oxy)tris(dimethylamino)phosphonium hexafluorophosphate[6] (190 mg, 0.5 mM). This mixture was degassed by three vacuum–argon atmosphere cycles. Acetonitrile (10 mL) was then added and the reaction mixture stirred under argon. After 45 min, the pale yellow solution was filtered through Celite in order to remove some traces of metallic palladium. Addition of triphenylphosphine (262 mg, 1 mM) followed by concentration of the reaction medium to ca. 2 mL and addition of 50 mL of dry ether led to the precipitation of a white solid. This suspension was stirred for 2 h, and then the solid was filtered off and washed with 3 × 10 mL of ether. The microcrystalline powder was dried under vacuum (yield 383 mg, 92%).

The same procedure was used with dichloromethane in place of acetonitrile.

Procedure II: (η^3-2-Methylallyl)bis(tetramethylthiourea)palladium(II) Hexafluorophosphate. In a 50-mL Schlenk tube were successively placed (η^3-2-methylallyl)chloropalladium(II) dimer (394 mg, 1 mM), tetramethylthiourea (529 mg, 4 mM), and finely powdered ammonium hexafluorophosphate (326 mg, 2 mM). The mixture was degassed by three vacuum–argon atmosphere cycles. Acetonitrile (10 mL) was then added and the reaction mixture stirred under argon. After 15 min, the suspended ammonium chloride was filtered off and the solution concentrated in vacuo to ca. 2 mL. Addition of ether (20 mL) led to the precipitation of the complex which was recovered by filtration and washed with 3 × 10 mL of ether. The microcrystalline powder was dried under vacuum (yield 1.01 g, 89%).

Acknowledgment. We thank the Dêlêgation Generale à la Recherche Scientifique et Technique and the Sociêtê des Produits Chimiques Ugine Kuhlmann for the support of this work.

Registry No. 6a, 74397-57-2; **6b**, 74397-58-3; **6c**, 74397-60-7; **6d**, 74397-62-9; **7a**, 74411-03-3; **7b**, 74397-64-1; **8a**, 74397-66-3; **8b**, 74397-67-4; **8c**, 74397-69-6; **8d**, 74397-71-0; $Pd_2(dba)_3$, 52409-22-0; (η^3-2-methylallyl)chloropalladium(II) dimer, 12081-18-4.

Contribution from the Department of Chemistry, Florida State University, Tallahassee, Florida 32306

Iron Carbonyl–Trifluorophosphine Compounds as Photocatalytic Precursors in Isomerization Studies

Grace L. Swartz and Ronald J. Clark*

Received April 2, 1980

Transition-metal carbonyls have long been studied as both stoichiometric and catalytically active species in organometallic reactions; their photochemistry has been actively investigated.[1,2] Soluble transition-metal catalysts offer the advantage of a definite stoichiometry and structure and have been used to elucidate catalytic reactions. The activity of the catalyst can be controlled by variation of the ligands attached to the metal atom, the oxidation state of the metal, or even the metal itself. Understanding the influence of these variables will allow the design of more efficient and more selective catalysts in the future, i.e., catalysts tailored for a given reaction.[3] Inorganic synthetic techniques are now available to afford compounds which will allow such systematic studies.

Several series of metal carbonyl–trifluorophosphine compounds, of the general form $M(PF_3)_y(CO)_x$, have been prepared and characterized. Phosphorus trifluoride is unique in the world of ligands that replace carbon monoxide in metal carbonyls in that its substitution reactions result in the sequential replacement of carbonyl groups throughout the entire composition range. When there can be more than one isomer for a given composition, all possible isomers will generally exist.

(10) Yamamoto, T.; Ishizu, J.; Yamamoto, A. *Chem. Lett.* **1979**, 1385.
(11) Postel, M.; Pfeffer, M.; Riess, J. *J. Am. Chem. Soc.* **1977**, *99*, 5623.
(12) Ittel, S. D.; Van-Catledge, F. A.; Jesson, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 6905.
(1) von Gustorf, E. A.; Leeders, L. H. G.; Fischler, I.; Perutz, R. *Adv. Inorg. Chem. Radiochem.* **1976**, *19*, 65–183.
(2) (a) Strohmeir, W. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 730–737. (b) Wrighton, M. *Chem. Rev.* **1974**, *74*, 401–430.
(3) Henrici-Olivê, G.; Olivê, S. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 105–115.

0020-1669/80/1319-3191$01.00/0