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bond in cyclometalated adducts may provide an essential step in which phenyl groups are transferred from silicon to platinum and, therefore, play a role in certain catalytic redistributions involving arylsilanes. Studies are currently underway to explore this possibility.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Louisiana Board of Regents for financial support.

Supplementary Material Available: Complete tables of experimental crystallographic data, positional parameters, bond lengths and angles, root-mean-square amplitudes of anisotropic displacement, torsion angles, and least-squares planes for **3** (17 pages); a listing of structure factors for **3** (50 pages). Ordering information is given on any current masthead page.

Synthesis and Properties of (π-Allyl)palladium Formates as Intermediates in Palladium-Catalyzed Reductive Cleavage of Allylic Acetates and Carbonates with Formic Acid

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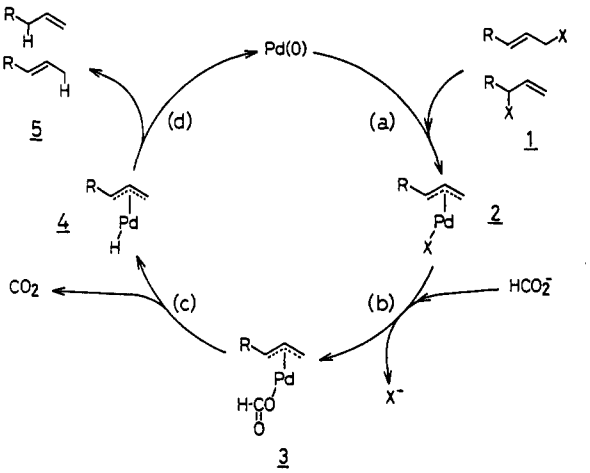
Summary: Neutral (π-allyl)(tertiary phosphine)palladium formates and ionic (π-allyl)bis(tertiary phosphine)palladium formates that are regarded as key intermediates in palladium-catalyzed reductive cleavage of allylic acetates and carbonates with formic acid have been prepared and characterized by ^1H and ^{13}C NMR spectroscopy. From a study of the formation process of these formate intermediates by anion exchange of the acetate anion with formic acid and by establishment of the course of liberation of olefins and CO_2 from the formate ligand, the validity of the proposed catalytic cycle has been substantiated.

Palladium-catalyzed reductive cleavage of allylic compounds, particularly acetates and carbonates, with formic acid provides a convenient synthetic means for regiospecific preparation of terminal olefins.[2,3] The catalytic cycle shown in Scheme I reasonably accounts for the course of the reductive-cleavage process. The cycle is constituted of (a) oxidative addition of the allylic substrate **1** to Pd(0) to give the allylic palladium acetate or carbonate **2**, (b) exchange of the anionic group with the formate group to give the allylic palladium formate **3**, (c) decarboxylation of the formate ligand to produce the allylic palladium hydride **4**, and (d) reductive elimination of the allylic and hydride ligands to liberate the olefin **5** with generation of the palladium(0) species that carries the catalytic cycle.

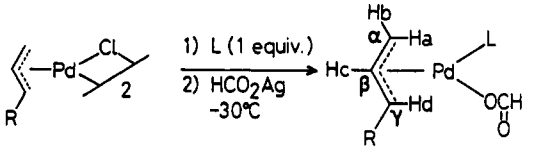
In the catalytic cycle the oxidative addition of allylic acetates is a well-established process.[4,5] Ready oxidative addition of the allylic carbonates to give a (π-allyl)palladium complex having two tertiary phosphine ligands and an ionic carbonate group also has been recently confirmed.[6] However, no study has been made on the preparation and characterization of the putative (π-allyl)palladium formates **3**, which serve as key intermediates in the reductive

Scheme I[a]



[a] X = OAc, OCO_2R, OPh, NO_2, etc. Supporting ligand(s) are omitted.

Scheme II



R = H **6a**
R = Me **6b**

L = $PMePh_2$ R = H **7a**
L = PMe_2Ph R = Me **7b**
L = $PMePh_2$ R = Me **7c**
L = P(o-tol)$_3$ R = Me **7d**

(1) (a) Waseda University. (b) Hokkaido University.

(2) (a) Hey, H.; Arpe, H.-J. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 928. (b) Tsuji, J.; Yamakawa, T. *Tetrahedron Lett.* **1979**, *7*, 613. (c) Tsuji, J.; Minami, I.; Shimizu, I. *Synthesis* **1986**, 623. (d) Ono, N.; Hamamoto, I.; Kamimura, A.; Kaji, A. *J. Org. Chem.* **1986**, *51*, 3734.

(3) Ram, S.; Ehrenkaufer, R. E. *Synthesis* **1988**, 91.

(4) (a) Yamamoto, T.; Akimoto, M.; Saito, O.; Yamamoto, A. *Organometallics* **1986**, *5*, 1559. (b) Yamamoto, T.; Akimoto, M.; Saito, O.; Yamamoto, A. *J. Am. Chem. Soc.* **1981**, *103*, 5600. (c) Hayashi, T.; Yamamoto, A.; Hagihara, T. *J. Org. Chem.* **1986**, *51*, 723. (d) Hayashi, T.; Hagihara, T.; Konishi, M.; Kumada, M. *J. Am. Chem. Soc.* **1983**, *105*, 7767.

(5) Palladium-catalyzed reaction of allylic compounds: (a) Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385–393. (b) Tsuji, J. *Organic Synthesis with Palladium Compounds*; Springer: Heidelberg, Germany, 1980. (c) Trost, B. M.; Verhoeven, T. R. *Comprehensive Organometallic Chemistry*; Pergamon Press: New York, 1982; Vol. 8, pp 799–938. (d) Tsuji, J. *Tetrahedron* **1986**, *42*, 4361–4401. (e) Auburn, P. R.; Mackenzie, P. B.; Bosnich, B. *J. Am. Chem. Soc.* **1985**, *107*, 2034. (f) Mackenzie, P. B.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1985**, *107*, 2046.

(6) The formation of ionic (π-allyl)palladium and -platinum complexes having two tertiary phosphine ligands and an alkyl carbonate anion has been also observed in the reaction of Pd(0) and Pt(0) complexes with alkyl carbonates: Ozawa, F.; Son, T.-I.; Ebina, S.; Osakada, K.; Yamamoto, A. To be submitted for publication. A part of the results was presented at the 3rd Anglo-Japanese Advanced Research Meeting on Organometallic Chemistry, Tokyo, Japan, 1990; abstract pp 97–98.

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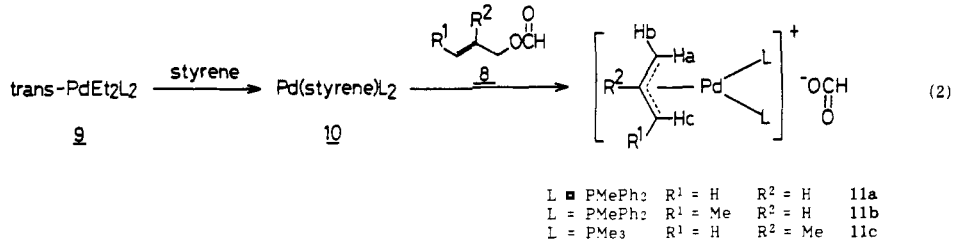
Scheme III



(2)

L = PMePh2 R1 = H R2 = H 11a
L = PMePh2 R1 = Me R2 = H 11b
L = PMe3 R1 = H R2 = Me 11c

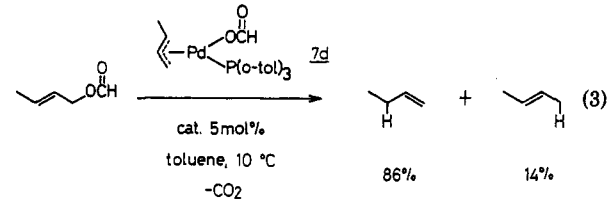
cleavage of the allylic acetates or carbonates with formic acid. We now report the synthesis and characterization of the (π-allyl)palladium formates and their decarboxylation process with regiospecific formation of the terminal olefins.

As intermediates in the catalytic cycle with formic acid, two types of allylic palladium formates are envisaged, one having one tertiary phosphine (**7**) and the other having two phosphine ligands (**11**) (see Schemes II and III). The former complex **7** was prepared by treating the (π-allyl)palladium chloride dimer **6**[7] with 1 equiv of a tertiary phosphine and silver formate[8] in toluene-d_8 at −30 °C.[9] The NMR spectra of the formate complexes **7** obtained showed that the formate ligand is coordinated with palladium at the site cis to the methyl-substituted terminus (C_γ) of the allylic ligand.

The other formate complex **11**, having two tertiary phosphine ligands, was prepared by oxidative addition of the allylic formates **8** to the styrene-coordinated Pd(0) complex **10** prepared in situ from diethylpalladium precursor **9**[10,11] (see Scheme III). Treatment of the Pd(0) complex **10** in THF at −20 °C with allylic formates **8** followed by removing the solvent and washing the residue with ether gave the ionic phosphine complexes **11** as white solids. Crystalline complex **11b** was obtained from THF–ether. Addition of 1 equiv of tertiary phosphine to **7** in toluene gave **11**.[12]

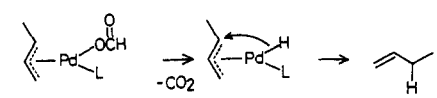
All the allylic palladium formate complexes **7** and **11** are thermally unstable and decompose rapidly at room temperature, liberating propene or butenes together with carbon dioxide as confirmed by ^{1}H NMR and/or GC analysis. The thermal decomposition of the (1-methylallyl)palladium formate complexes having one or two tertiary phosphine ligands is first order in the formate complex. The thermolysis of the P(*o*-tol)$_3$-coordinated complex **7d** gave 1-butene predominantly (91%) together with a small amount of 2-butene (9%) with a rate constant of 3.1×10^{-4} at 10 °C. The thermolysis was not hindered by added P(*o*-tol)$_3$ (2–3 equiv). The product ratio was not affected by addition of the ligand. The formation of 1-butene was less specific with the PMe_2Ph-coordinated complex **7b**, which liberated 1-butene and 2-butene in an about equal ratio.

The isolated mono- and bis(phosphine) complexes proved to be catalytically active for reductive cleavage of (*E*)-2-butenyl formate to give mainly 1-butene and a minor amount of 2-butene (eq 3). Butenes in a ratio similar to that observed in the thermolysis of the (π-allyl)palladium formate complex **7d** were liberated in the catalytic reaction.



(3)

These results strongly indicate that the (π-allyl)palladium formate complexes are involved in the catalytic cycle as shown in Scheme I and also in the catalytic decarboxylation of the allylic formates. For production of 1-butene from the (1-methylallyl)palladium formate complexes **7b–d** having one phosphine ligand at the position trans to the substituted side in the 1-methylallyl ligand, decarboxylation of the formate ligand probably proceeds with retention of the stereochemistry around palladium.[13] The ensuing reductive elimination of the 1-methylallyl and the hydride ligand thus formed would liberate mainly 1-butene as shown in eq 4. The nature of the tertiary phosphine ligand employed delicately influences the product distribution of butenes, as will be reported later.



(4)

After establishment of the process (a) and (c) + (d) in Scheme I the remaining problem in supporting the validity of the proposed Scheme I for the catalytic conversion of

(7) Dent, W. T.; Long, R.; Wilkinson, A. J. *J. Chem. Soc.* **1964**, 1585.

(8) Silver formate was prepared from formic acid and silver carbonate. Silver carbonate was added to excess formic acid at 0 °C, and the mixture was stirred for 30 min at 0 °C in the dark. Addition of ether caused formation of a white solid, which was filtered, washed with ether, and dried in vacuo to give AgOCHO, which was used without purification.

(9) NMR spectra of the (π-allyl)palladium formates **7a–d** are as follows. **7a**: ^{1}H NMR (400 MHz, toluene-d_8, −30 °C, in ppm from internal Me_4Si) δ 8.98 (s, 1 H, OCHO), 4.90 (m, 1 H, H_c), 4.54 (t, J = 7.0 Hz, 1 H, H_d), 3.78 (dd, J = 13.9, 9.5 Hz, 1 H, H_a), 2.57 (d, J = 4.8 Hz, 1 H, H_b), 2.09 (1 H, H_a), 1.67 (d, J = 9.5 Hz, 3 H, PMe); ^{31}P NMR (162 MHz, toluene-d_8, −20 °C, in ppm from internal 85% D_3PO_4 in D_2O) δ 10.8 (s); ^{13}C NMR (100.5 MHz, toluene-d_8, −30 °C, in ppm from internal Me_4Si) δ 167.5 (OCHO), 117.6 (J_{C-P} = 4.9 Hz, C_β), 77.7 (J_{C-P} = 28.4 Hz, C_γ), 51.2 (C_α), 12.8 (J = 25.4 Hz, PMe). **7b**: ^{1}H NMR (400 MHz, toluene-d_8, −20 °C) δ 8.97 (s, 1 H, OCHO), 4.80 (m, 1 H, H_c), 4.64 (qdd, J = 6.2 Hz, 1 H, H_d), 2.51 (m, 1 H, H_b), 2.04 (m, 1 H, H_a), 1.52 (dd, J = 8.8, 6.2 Hz, 3 H, $CHCH_3$), 1.29 (d, J = 9.2 Hz, 6 H, PMe_2). **7c**: ^{1}H NMR (400 MHz, toluene-d_8, −30 °C) δ 8.97 (s, 1 H, OCHO), 4.70 (m, 1 H, H_c), 4.46 (qdd, J = 6.2 Hz, 1 H, H_d), 2.42 (m, 1 H, H_b), 1.93 (m, 1 H, H_a), 1.71 (d, J = 8.8 Hz, 3 H, $CHCH_3$), 1.52 (dd, J = 8.8, 6.3 Hz, 3 H, PMe); ^{13}C NMR (100.5 MHz, toluene-d_8, −30 °C) δ 167.0 (OCHO), 116.2 (J_{C-P} = 4.4 Hz, C_β), 96.1 (J_{C-P} = 27.2 Hz, C_γ), 44.3 (C_α), 17.5 (J = 3.7 Hz, CH_3), 14.0 (J_{C-P} = 25.0 Hz, PMe). **7d**: ^{1}H NMR (400 MHz, toluene-d_8, −60 °C) δ 8.82 (s, 1 H, OCHO), 4.94 (m, 1, H, H_c), 4.80 (m, 1 H, H_d), 2.42 (bs, 3 H, C_6H_4Me), 1.54 (t, J = 6.96 Hz, 3 H, $CHCH_3$).

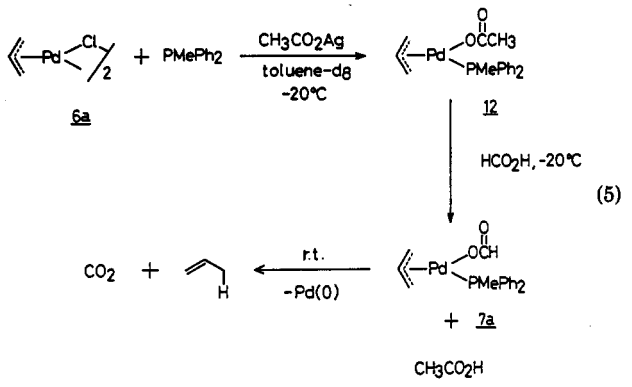
(10) Ozawa, F.; Ito, T.; Nakamura, Y.; Yamamoto, A. *J. Organomet. Chem.* **1979**, *168*, 375.

(11) NMR spectra of the (π-allyl)palladium formates **11a–c** are as follows. **11a**: ^{1}H NMR (400 MHz, $CDCl_3$, −20 °C) δ 8.90 (s, 1 H, OCHO), 5.73 (m, 1 H, H_c), 4.00 (m, 2 H, H_b), 3.60 (m, 2 H, H_a); ^{31}P NMR (162 MHz, $CDCl_3$, −20 °C) δ 8.62 (s). **11b**: ^{1}H NMR (400 MHz, $CDCl_3$, −20 °C) δ 8.89 (s, 1 H, OCHO), 5.45 (m, 1 H, H_c), 4.34 (m, 1 H, H_d), 3.60 (m, 1 H, H_b), 3.3–3.4 (m, 1 H, H_a); ^{13}C NMR (100.5 MHz, $CDCl_3$, −20 °C) δ 168.4 (OCHO), 113.9 (C_β), 66.0, 17.0, 15.3. **11c**: ^{1}H NMR (400 MHz, acetone-d_6, −40 °C) δ 8.56 (s, 1 H, OCHO), 4.23 (bs, 1 H, H_a), 3.12 (virtual triplet, J = 5.5 Hz, 1 H, H_b), 1.77 (s, 3 H, Me), 1.65 (virtual triplet, J = 5.1 Hz, 3 H, P*Me*); ^{13}C NMR (100.5 MHz, acetone-d_6, −40 °C) δ 167.1 (OCHO), 137.11 (t, J = 5.1 Hz), 69.7 (t, J = 15.8 Hz), 23.8 (C*Me*), 17.2 (dd, J = 16.1, 14.0 Hz); ^{31}P NMR (162 MHz, acetone-d_6, −40 °C) δ −15.9 (s).

(12) A similar transformation of (π-allyl)PdCl(L) to [(π-allyl)Pd(L)$_2$]$^+$Cl$^-$ has been reported: Vrieze, K.; Praat, A. P.; Cossee, P. *J. Organomet. Chem.* **1968**, *12*, 533.

(13) Merrifield, J. H.; Gladysz, J. A. *Organometallics* **1983**, *2*, 782.

allylic acetate into terminal olefins is the feasibility of the displacement of the acetate group by the formate group. For an examination of the process, the (π-allyl)(diphenylmethylphosphine)palladium acetate complex **12** was prepared by a process similar to that employed for the formate complex **7a** with the use of silver acetate instead of silver formate in eq 5.[14] Spectroscopic examination of



(5)

the change of the ^{1}H NMR spectrum on addition of formic acid to the toluene solution containing **12** indeed indicated the displacement of the acetate ligand by the formate ligand with liberation of acetic acid and production of the (π-allyl)palladium formate complex **7a** at −20 °C. Warming the solution led to liberation of propene, as was observed in the thermal decomposition of the isolated complex **7a**.

In conclusion, key intermediate complexes shown in Scheme I, except for the (π-allyl)palladium hydride complex **4**, which apparently is quite unstable,[15] have been identified in the present study in support of the validity of the proposed reaction mechanism. The influence of tertiary phosphine ligands on the course of reductive cleavage of the allylic substrates is presently under investigation.

Registry No. 6a, 12012-95-2; **6b**, 132884-87-8; **7a**, 132884-83-4; **7b**, 132884-84-5; **7c**, 132884-85-6; **7d**, 132884-86-7; **8a**, 1838-59-1; **8b**, 132884-82-3; **8c**, 820-57-5; **9** (L = $PMePh_2$), 132957-78-9; **9** (L = PMe_3), 132957-79-0; **11a**, 132884-89-0; **11b**, 132884-91-4; **11c**, 132884-93-6; **12**, 132884-94-7; 1-butene, 106-98-9; 2-butene, 624-64-6; styrene, 100-42-5.

(14) NMR spectra of **12**: ^{1}H NMR (400 MHz, toluene-d_8, −20 °C) δ 5.07 (m, 1 H, H_c), 4.49 (t, J = 7.0 Hz, 1 H, R = H), 3.77 (dd, J = 13.9, 9.5 Hz, 1 H, H_d), 2.51 (dd, J = 13.2, 7.0 Hz, 1 H, H_b), 2.18 (b s, 3 H, CH_3CO_2–).

(15) For an analogous (π-allyl)platinum hydride formation of propene has been confirmed: Bertani, R.; Carturan, G.; Scrivanti, A. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 246.

Aqueous Organometallic Chemistry: Synthesis and Structure of Chloro[(1–3-η:6–8-η)-2,7-dimethyloctadienediyl](semicarbazide)-ruthenium(IV) Chloride Dihydrate

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Summary: The first example of a water-soluble cationic Ru(IV) complex with two η^3-allyl functions has been isolated and characterized by an X-ray crystal structure study. The Ru ion is at the center of a distorted trigonal bipyramid where the equatorial donors are two η^3-allyl functions and a terminal semicarbazide N. The O of the semicarbazide and Cl reside in the axial positions.

We wish to report our discovery and characterization of a unique cation that can provide a convenient entry into aqueous high formal oxidation state organometallic chemistry. There is current interest in both water-soluble organometallic compounds for various catalytic reactions[1] and organometallic compounds with high formal oxidation states.[2] Organometallic compounds were generally considered to require low formal oxidation states, but this perception is disappearing. The recent discovery of an aqueous ring-opening metathesis polymerization reaction[3] is only one of the new areas of aqueous organometallic chemistry, even though the species involved were neither isolated nor identified.

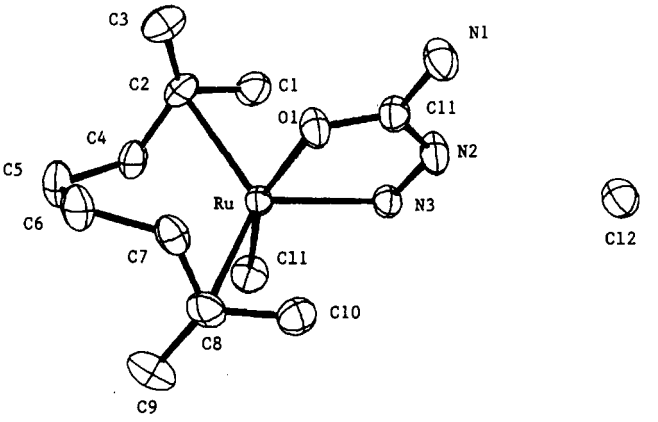

Figure 1. View of chloro[(1–3-η:6–8-η)-2,7-dimethyloctadienediyl](semicarbazide)ruthenium(IV) chloride showing the atomic numbering with the thermal ellipsoids drawn at the 50% probability level.

As part of a continuing study of the reactions of DAPSC, 2,6-diacetylpyridine-disemicarbazone, with various metal ions of the second and third row,[4] we reacted DAPSC with

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(1) Fache, E.; Senocq, F.; Santini, C.; Basset, J.-M. *J. Chem. Soc., Chem. Commun.* **1990**, 1776. Chan, T. C.; Li, C.-J. *Organometallics* **1990**, *9*, 2649. Light, J.; Breslow, R. *Tetrahedron Lett.* **1990**, *31*, 2957 and references therein.

(2) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1297. Herrmann, W. A. *Comments Inorg. Chem.* **1988**, 73.

(3) Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 7542.

(4) Wester, D. W.; Palenik, G. J. *J. Am. Chem. Soc.* **1973**, *95*, 6505. Wester, D. W.; Palenik, G. J. *J. Am. Chem. Soc.* **1974**, *96*, 7576. Palenik, G. J.; Wester, D. W.; Rychlewska, U.; Palenik, R. C. *Inorg. Chem.* **1976**, *15*, 1814. Thomas, J. E.; Palenik, G. J. *Inorg. Chim. Acta* **1980**, *44*, L303. Thomas, J. E. M.S. Dissertation, University of Florida, Gainesville, FL, 1980.

0276-7333/91/2310-1223$02.50/0