step which becomes 4 times faster than in the presence of the alkali metal cations. This is in agreement with the fact that the reaction of the second step involves a 4^- ion, so that both the electrostatic and the nonelectrostatic effects are magnified.

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Conformational Studies of Bridging Carboxylate Complexes of Palladium(II) and Platinum(II)

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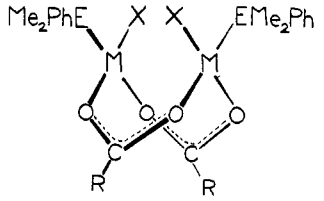
A series of bridging *cis*-di-μ-carboxylate complexes of palladium(II) and platinum(II) of the general types $[X(Me_2PhE)M(O_2CR)]_2$ and $[X_2(Me_2PhE)_2M_2[O_2C(CH_2)_nCO_2]]$ (X = Cl, Br, I; E = P, As; M = Pd, Pt; R = CH_3, CH_2Cl, CH_2Br, CF_3, CCl_3, CMe_3, CPh_3; n = 3–8) have been synthesized and structurally characterized. The dynamic stereochemistry of these complexes has been investigated using variable-temperature nmr techniques. The $\Delta G^{\mp}$ of the process whereby the stereochemically nonequivalent methyl groups of the coordinated Me_2PhE ligand become magnetically equivalent is dependent on metal substituents, carboxylate substituents, and the solvent. The exchange process has low activation energies (3–6 kcal/mol) and large negative entropies of activation (−20 to −40 eu). The results obtained indicate that the exchange mechanism involves the rapid solvolysis of a metal–carboxylate bond to give a mono-μ-carboxylate intermediate rather than a simple inversion of the $Pd_2C_2O_4$ ring. The structurally analogous *cis*-di-μ-1,3-diphenyltriazene complex $[Cl(Me_2PhP)Pd(Ph_2N_3)]_2$ did not undergo such exchange reactions. The exchange processes occurring in π-allylic palladium carboxylates have been reinvestigated and the rates found to be markedly affected by the solvent.

Introduction

Recently, π-allylic palladium acetate dimers have been shown by ^1H nmr spectroscopy to exist as a mixture of two conformational isomers in chloroform solution.[1,2] The temperature dependence of their ^1H nmr spectra has been interpreted in terms of a rapid intramolecular process which leads to nmr equivalence of nonequivalent π-allylic groups in the nonsymmetrical isomer together with a rapid bimolecular process which is operative at higher temperatures and which leads to nmr equivalence of the conformational isomers. It has been suggested that the intramolecular process be ascribed to a rapid boat → chair → boat conformational isomerism of the $Pd_2O_4C_2$ ring. The geometrically similar π-allylic palladium 1,3 diphenyltriazenide dimers have also been shown to exist in solution as two conformational isomers.[3] In contrast to the carboxylate complexes, no evidence for rapid intramolecular or intermolecular exchange processes was observed for these complexes, their nmr spectra being temperature independent from −60 to +30° in $CDCl_3$ and from +50 to +110° in $CHBr_3$.

In an effort to clarify the nature of the apparent intramolecular process observed in the π-allylic palladium carboxylate systems we have succeeded in synthesizing a series of di-μ-carboxylate complexes of general formulas $[(Me_2PhE)XM(OOCR)]_2$ and structure I (E = P, As; M = Pd, Pt; X = Cl, Br, I; R = CH_3, CH_2Cl, CH_2Br, CCl_3, CF_3, CMe_3, CPh_3) from the reaction of the appropriate bridged halide dimer with 2 mol of a silver carboxylate salt in chloroform: $[(Me_2PhE)MX_2]_2 + 2AgOOCR \rightarrow I + 2AgX\downarrow$.



I

In the absence of any exchange, a molecule of structure I should give two methyl proton resonances of equal intensities in the ^1H nmr spectrum assignable to nonequivalent methyl groups on the Me_2PhE ligand (there is no plane of symmetry passing through the E–M axis). However any rapid process which effectively inverts the boat conformation of the $Pd_2O_4C_2$ ring of I will also interchange the nonequivalent methyl groups of the Me_2PhE ligands and as such will be amenable to variable-temperature nmr studies. In this paper we report the synthesis and structural characterization of complexes of type I and some related complexes, and discuss the mechanistic implications of the temperature dependence of their ^1H nmr spectra.

Experimental Section

Preparation of Compounds.—Bridging halide complexes of the type $[(Me_2PhE)MX_2]_2$ were prepared by the method of Jenkins and Shaw.[4] Dimethylphenylphosphine and dimethylphenylarsine were synthesized in the general manner described elsewhere.[5]

Di-μ-acetato-dichlorobis(dimethylphenylphosphine)dipalladium(II).—A solution of di-μ-chloro-dichlorobis(dimethylphenylphos-

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(2) P. W. N. M. Van Leeuwen and A. P. Praat, *Recl. Trav. Chim. Pays-Bas*, **89**, 321 (1970).

(3) J. Powell and T. Jack, *J. Organometal. Chem.*, **27**, 133 (1971).

(4) J. M. Jenkins, and B. L. Shaw, *J. Chem. Soc. A*, 770 (1966).

(5) D. Adams and J. Raynor, "Advanced Practical Inorganic Chemistry," Wiley, New York, N. Y., 1965, p 117.

phine)dipalladium(II) (0.86 g) in chloroform (40 ml) and silver acetate (0.48 g) was shaken for 1 hr. The reaction mixture was filtered to remove insoluble silver salts, and the orange filtrate was evaporated to dryness under reduced pressure. The orange solid residue recrystallized from chloroform–petroleum ether (bp 30–60°) as orange prisms; yield 0.81 g (87%), mp 135–142°. *Anal.* Calcd for $C_{20}H_{28}Cl_2O_4P_2Pd_2$: C, 35.43; H, 4.16. Found: C, 35.53; H, 4.29.

The following compounds were prepared in a similar manner by shaking the appropriate bridging halide dimer with the silver salt in chloroform until reaction was complete (1–30 hr).

Di-μ-acetato-dibromobis(dimethylphenylphosphine)dipalladium(II).—Orange needles, 94%, mp 165–169°. *Anal.* Calcd for $C_{20}H_{28}Br_2O_4P_2Pd_2$: C, 31.32; H, 3.67. Found: C, 31.70; H, 3.74.

Di-μ-acetato-diiodobis(dimethylphenylphosphine)dipalladium(II).—Orange needles, 82%, mp 141–146°. *Anal.* Calcd for $C_{20}H_{28}I_2O_4P_2Pd_2$: C, 27.90; H, 3.27; mol wt 861. Found: C, 28.27; H, 3.22; mol wt (osmometrically in 2.0% w/v chloroform solution) 886.

Di-μ-monochloroacetato-dichlorobis(dimethylphenylphosphine)dipalladium(II).—Orange needles, 83%, mp 161–171°. *Anal.* Calcd for $C_{20}H_{26}Cl_4O_4P_2Pd_2$: C, 32.16; H, 3.51. Found: C, 31.93; H, 3.71.

Di-μ-monochloroacetato-dibromobis(dimethylphenylphosphine)dipalladium(II).—Orange prisms, 84%, mp 155–163°. *Anal.* Calcd for $C_{20}H_{26}Br_2Cl_2O_4P_2Pd_2$: C, 28.73; H, 3.13. Found: C, 28.33; H, 3.04.

Di-μ-monochloroacetato-diiodobis(dimethylphenylphosphine)dipalladium(II).—Red plates, 70%, mp 141–144°. *Anal.* Calcd for $C_{20}H_{26}Cl_2I_2O_4P_2Pd_2$: C, 25.83; H, 2.82. Found: C, 25.60; H, 2.84.

Di-μ-trifluoroacetatato-dichlorobis(dimethylphenylphosphine)dipalladium(II).—Orange needles, 82%, mp 164–170°. *Anal.* Calcd for $C_{20}H_{22}Cl_2F_6O_4P_2Pd_2$: C, 30.58; H, 2.82. Found: C, 30.51; H, 2.54.

Di-μ-trifluoroacetato-dibromobis(dimethylphenylphosphine)dipalladium(II).—Orange needles, 78%, mp 169–178°. *Anal.* Calcd for $C_{20}H_{22}Br_2F_6O_4P_2Pd_2$: C, 27.46; H, 2.54. Found: C, 27.29; H, 2.76.

Di-μ-trifluoroacetato-diiodobis(dimethylphenylphosphine)dipalladium(II).—Red needles, 86%, mp 145–148°. *Anal.* Calcd for $C_{20}H_{22}F_6I_2O_4P_2Pd_2$: C, 24.79; H, 2.79. Found: C, 25.02; H, 2.44.

Di-μ-trimethylacetato-dichlorobis(dimethylphenylphosphine)dipalladium(II).—Orange prisms, 73%, mp 180–186°. *Anal.* Calcd for $C_{26}H_{40}Cl_2O_4P_2Pd_2$: C, 40.97; H, 5.29. Found: C, 40.75; H, 5.20.

Di-μ-trimethylacetato-dibromobis(dimethylphenylphosphine)dipalladium(II).—Orange prisms, 64%, mp 179–181.5°. *Anal.* Calcd for $C_{26}H_{40}Br_2O_4P_2Pd_2$: C, 36.68; H, 4.74. Found: C, 36.44; H, 4.76.

Di-μ-trimethylacetato-diiodobis(dimethylphenylphosphine)dipalladium(II).—Orange prisms, 60%, mp 164–168° dec. *Anal.* Calcd for $C_{26}H_{40}I_2O_4P_2Pd_2$: C, 33.04; H, 4.27. Found: C, 33.37; H, 4.40.

Di-μ-triphenylacetato-dichlorobis(dimethylphenylphosphine)dipalladium(II).—Orange prisms, 90%, mp 156–159°. *Anal.* Calcd for $C_{56}H_{52}Cl_2O_4P_2Pd_2 \cdot CHCl_3$: C, 54.56; H, 4.26. Found: C, 54.50; H, 4.49.

Di-μ-trichloroacetato-dichlorobis(dimethylphenylphosphine)dipalladium(II).—Orange plates, 85%, mp 129–135°. *Anal.* Calcd for $C_{20}H_{22}Cl_8O_4P_2Pd_2$: C, 27.21; H, 2.51. Found: C, 27.18; H, 2.60.

Di-μ-monobromoacetato-dichlorobis(dimethylphenylphosphine)dipalladium(II).—Orange prisms, 74%, mp 163–166°. *Anal.* Calcd for $C_{20}H_{26}Br_2Cl_2O_4P_2Pd_2$: C, 28.74; H, 3.13. Found: C, 29.02; H, 2.99.

Di-μ-acetato-dichlorobis(dimethylphenylarsine)dipalladium(II).—Red needles, 50%, mp 174–179°. *Anal.* Calcd for $C_{20}H_{28}As_2Cl_2O_4Pd_2$: C, 31.37; H, 3.66. Found: C, 31.37; H, 3.76.

Di-μ-acetato-dibromobis(dimethylphenylarsine)dipalladium(II).—Red needles, 73%, mp 169–177°. *Anal.* Calcd for $C_{20}H_{28}As_2Br_2O_4Pd_2$: C, 28.08; H, 3.30. Found: C, 28.15; H, 3.41.

Di-μ-acetato-diiodobis(dimethylphenylarsine)dipalladium(II).—Red needles, 78%, mp 124–128°. *Anal.* Calcd for $C_{20}H_{28}As_2I_2O_4Pd_2$: C, 25.30; H, 2.97. Found: C, 25.09; H, 3.03.

Di-μ-monochloroacetato-dichlorobis(dimethylphenylarsine)dipalladium(II).—Red needles, 75%, mp 187–189°. *Anal.* Calcd for $C_{20}H_{26}As_2Cl_4O_4Pd_2$: C, 28.84; H, 3.14; mol wt 832.8. Found: C, 28.57; H, 3.05; mol wt (osmometrically in 2% w/v chloroform solution) 805.

Di-μ-monochloroacetato-dibromobis(dimethylphenylarsine)dipalladium(II).—Red prisms, 69%, mp 138–141°. *Anal.* Calcd for $C_{20}H_{26}As_2Br_2Cl_2O_4Pd_2$: C, 26.56; H, 2.90. Found: C, 26.53; H, 2.76.

Di-μ-monochloroacetato-diiodobis(dimethylphenylarsine)dipalladium(II).—Red plates, 50%, mp 89–90°. *Anal.* Calcd for $C_{20}H_{26}As_2Cl_2O_4Pd_2$: C, 23.65; H, 2.58. Found: C, 23.69; H, 2.73.

μ,μ-Azelato-dichlorobis(dimethylphenylphosphine)dipalladium(II).—Yellow solid, 90%, mp 165–166°. *Anal.* Calcd for $C_{25}H_{36}Cl_2O_4P_2Pd_2$: C, 40.24; H, 4.86; mol wt 746. Found: C, 39.68; H, 4.87; mol wt (osmometrically in 1.1% w/v chloroform solution) 892.

μ,μ-Suberato-dichlorobis(dimethylphenylphosphine)dipalladium(II).—Yellow solid, 90%, mp 143–148°. *Anal.* Calcd for $C_{24}H_{34}Cl_2O_4P_2Pd_2 \cdot 0.5CHCl_3$: C, 37.15; H, 4.39; mol wt 732. Found: C, 37.05; H, 4.68; mol wt (osmometrically in 0.6% w/v chloroform solution) 955.

μ,μ-Adipato-dichlorobis(dimethylphenylphosphine)dipalladium(II).—Yellow solid, 90%, mp 163–174°. *Anal.* Calcd for $C_{22}H_{30}Cl_2O_4P_2Pd_2$: C, 37.52; H, 4.29; mol wt 704. Found: C, 37.80; H, 4.30; mol wt (osmometrically in 0.2% w/v chloroform solution) 1190.

μ,μ-Sebacato-dichlorobis(dimethylphenylphosphine)dipalladium(II).—Orange prisms, 82%, mp 167–172°. *Anal.* Calcd for $C_{26}H_{38}Cl_2O_4P_2Pd_2$: C, 41.08; H, 5.04; mol wt 760. Found: C, 41.18; H, 5.24; mol wt (osmometrically in 1.3% w/v chloroform solution) 766.

Di-μ-acetato-dichlorobis(dimethylphenylphosphine)diplatinum(II).—Yellow needles, 81%, mp 110–116°. *Anal.* Calcd for $C_{20}H_{28}Cl_2P_2O_4Pt_2$: C, 28.08; H, 3.30; mol wt 944. Found: C, 28.29; H, 3.39; mol wt (osmometrically in 2.3% w/v chloroform solution) 964.

Di-μ-acetato-dibromobis(dimethylphenylphosphine)diplatinum(II).—Yellow needles, 60%, mp 187–190°. *Anal.* Calcd for $C_{20}H_{28}Br_2O_4P_2Pt_2$: C, 25.44; H, 2.99. Found: C, 26.00; H, 3.13.

Di-μ-acetato-diiodobis(dimethylphenylphosphine)diplatinum(II).—Orange needles, 50%, mp 151–155°. *Anal.* Calcd for $C_{20}H_{28}I_2O_4P_2Pt_2$: C, 23.13; H, 2.72. Found: C, 23.18; H, 2.72.

Di-μ-monochloroacetato-dichlorobis(dimethylphenylphosphine)diplatinum(II).—Yellow prisms, 68%, mp 169–177°. *Anal.* Calcd for $C_{20}H_{26}Cl_4O_4P_2Pt_2$: C, 25.99; H, 2.84. Found: C, 26.27; H, 3.11.

Di-μ-trifluoroacetato-dichlorobis(dimethylphenylphosphine)diplatinum(II).—Orange needles, 80%, mp 172–179°. *Anal.* Calcd for $C_{20}H_{22}Cl_2F_6O_4P_2Pt_2$: C, 24.93; H, 2.30. Found: C, 24.99; H, 2.41.

Di-μ-acetato-dichlorobis(dimethylphenylarsine)diplatinum(II).—Amber prisms, 20%, mp 158–187°. *Anal.* Calcd for $C_{20}H_{28}As_2Cl_2O_4Pt_2$: C, 25.45; H, 2.99. Found: C, 25.40; H, 2.92.

Di-μ-acetato-dibromobis(dimethylphenylarsine)diplatinum(II).—Orange prisms, 64%, mp 183–184°. *Anal.* Calcd for $C_{20}H_{28}As_2Br_2O_4Pt_2$: C, 23.26; H, 2.73. Found: C, 23.44; H, 2.74.

Di-μ-acetato-diiodobis(dimethylphenylarsine)diplatinum(II).—Orange needles, 53%, mp 135–137°. *Anal.* Calcd for $C_{20}H_{28}As_2I_2O_4Pt_2$: C, 21.31; H, 2.50. Found: C, 21.41; H, 2.59.

μ,μ-Sebacato-dichlorobis(dimethylphenylphosphine)diplatinum(II).—Yellow solid, 85%, mp 180–185°. *Anal.* Calcd for $C_{26}H_{38}Cl_2O_4P_2Pt_2$: C, 33.30; H, 4.08; mol wt 937. Found: C, 33.31; H, 4.11; mol wt (osmometrically in 1.0% w/v chloroform solution) 950.

Di-μ-1,3-diphenyltriazenido-dichlorobis(dimethylphenylphosphine)dipalladium(II).—A solution of di-μ-acetato-dichlorobis(dimethylphenylphosphine)dipalladium(II) (0.43 g) in chloroform (8 ml) was added to a solution of diazoaminobenzene (0.26 g) in chloroform (5 ml). The solvent was removed under reduced pressure to leave a red oil, which was placed *in vacuo* for 24 hr to remove acetic acid. The residual red glass was recrystallized from chloroform–petroleum ether (bp 30–60°) to give orange prisms; yield 0.38 g (63%); mp 249–250°. *Anal.* Calcd for $C_{40}H_{42}Cl_2N_6P_2Pd_2$: C, 50.46; H, 4.42; mol wt 954. Found: C, 50.23; H, 4.56; mol wt (osmometrically in 0.8% w/v chloroform solution) 935.

Di-μ-1-methyl-3-phenyltriazenido-dichlorobis(dimethylphenylphosphine)dipalladium(II).—Solid 1-methyl-3-phenyltriazene (0.13 g) was added to a solution of di-μ-acetato-dichlorobis(di-

TABLE I

NMR SPECTRAL DATA IN THE REGION OF FAST EXCHANGE ($CHCl_3$ SOLUTION;[a] 60 MHz)

COMPOUND	PROTON RESONANCES		COUPLING CONSTANTS			VARIABLE TEMPERATURE DATA			INFRARED DATA	
	$PhMe_2P$ METHYL PROTONS	CARBOXYLATE BRIDGE PROTONS	$PhMe_2P$ METHYL PROTONS $J_{31_{P-H}}$	$PhMe_2P$ METHYL PROTONS $J_{195_{Pt-H}}$	CARBOXYLATE BRIDGE PROTONS $J_{195_{Pt-H}}$	$\Delta\nu_0$ (cps)[b]	T_c (°C)[b]	$\Delta G^{\ddagger}_{T_c}$ (kcal/mole)[b]	ν_{ASYM} (C – O) (cm^{-1})	ν_{SYMM} (C – O) (cm^{-1})
$[(PhMe_2P)ClPd(OOCCH_3)]_2$	8.10	8.20	13.4			14.7 ± 3.0	+12.4 ± 1.0	14.8 ± 0.3	1575 (s)	1418 (s)
$[(PhMe_2P)BrPd(OOCCH_3)]_2$	8.00	8.14	13.3			23.8	+27.5	15.2	1580 (s)	1413 (s)
$[(PhMe_2P)IPd(OOCCH_3)]_2$	7.83	8.11	12.5			41.0	+24.3	14.7	1575 (s)	1412 (s)
$[(PhMe_2P)ClPd(OOCCH_2Cl)_2]$	8.12	6.27	13.9			13.0	- 2.7	14.0	1601 (s)	1391 (s)
$[(PhMe_2P)BrPd(OOCCH_2Cl)_2]$	7.95	6.20	13.3			21.8	+ 4.2	14.1	1600 (s)	1392 (m)
$[(PhMe_2P)IPd(OOCCH_2Cl)_2]$	7.82	6.14	12.9			39.5	- 7.1	13.1	1600 (s)	1395 (s)
$[(PhMe_2P)ClPd(OOCCF_3)]_2$	8.11		13.8			15.6	-23.2	12.8	1659 (s)	1445, 1458 (m) (?)
$[(PhMe_2P)BrPd(OOCCF_3)]_2$	8.00		13.5			44.8[c,j]	- 9.1[c]	13.0[c]	1660 (s)	1442, 1452 (m) (?)
$[(PhMe_2P)IPd(OOCCF_3)]_2$	7.85		13.0			45.9	-25.2	12.1	1660 (s)	1440, 1450 (m) (?)
$[(PhMe_2P)ClPd(OOCCCl_3)]_2$	8.11		13.8			15.5	-27.1	12.6	1642 (s)	1360 (s)
$[(PhMe_2P)ClPd(OOCCMe_3)]_2$	8.09	9.01	13.8			29.2[c]	+30.5[c]	15.3[c]	1560 (s)	1408 (m)
$[(PhMe_2P)BrPd(OOCCMe_3)]_2$	8.00	9.00	13.2			25.1	+34.2	15.5	1560 (s)	1412 (s)
$[(PhMe_2P)IPd(OOCCMe_3)]_2$	7.90	8.90	12.8			61.0[c,i]	+23.8[c]	14.5[c]	1552 (s)	1410 (s)
$[(PhMe_2P)ClPd(OOCCH_2Br)]_2$	8.08	6.40	13.5			12.5	- 6.5	13.8	1590 (s)	1380 (s)
$[(PhMe_2P)ClPd(OOCCPh_3)]_2$	8.66		13.4			90.5[d]	+83.0[d]	17.2[d]	1578 (s)	1360 (s)
$[(PhMe_2As)ClPd(OOCCH_3)]_2$	8.29	8.26				17.6[c]	+14.3[c]	14.7[c]	1560 (s)	1405 (m)
$[(PhMe_2As)BrPd(OOCCH_3)]_2$	8.20	8.20				17.7	+10.6	14.5	1555 (s)	1398 (s)
$[(PhMe_2As)IPd(OOCCH_3)]_2$	7.98	8.11				29.6	+13.4	14.4	1558 (s)	1402 (s)
$[(PhMe_2As)ClPd(OOCCH_2Cl)_2]$	8.23	6.29				8.0	-13.6	13.6	1600 (s)	1402 (s)
$[(PhMe_2As)BrPd(OOCCH_2Cl)_2]$	8.11	6.22				14.5	-13.9	13.3	1600 (s)	1400 (s)
$[(PhMe_2As)IPd(OOCCH_2Cl)_2]$	7.95	6.19				25.7	- 8.3	13.3	1600 (s)	1400 (s)
$[(PhMe_2P)_2Cl_2Pd_2OOC(CH_2)_7COO]$	8.15	——[g]	13.9			14.2	+26.1	15.5	1565 (s)	1405 (s)
$[(PhMe_2P)_2Cl_2Pd_2OOC(CH_2)_8COO]$	8.13	——[g]	13.0			13.1	+33.5	15.9	1565 (s)	1410 (m)
$[(PhMe_2P)ClPt(OOCCH_3)]_2$	8.16	8.16	12.6	34.5[e]	2.8	23.9[c]	+21.6	14.9[c]	1575 (s)	1420 (s)
$[(PhMe_2P)BrPt(OOCCH_3)]_2$	8.12	8.11	12.8	33.5[e]	2.8	23.5	+29.5	15.3	1578 (s)	1418 (s)
$[(PhMe_2P)IPt(OOCCH_3)]_2$	7.94	8.07	12.5	33.6[e]	2.8	36.6	+31.6	15.2	1570 (s)	1420 (s)
$[(PhMe_2P)ClPt(OOCCH_2Cl)_2]$	8.13	6.22	12.6	35.2	——	20.4[c]	+ 0.5[c]	13.9[c]	1605 (s)	1410 (s)
$[(PhMe_2P)ClPt(OOCCF_3)]_2$	8.13		12.7	35.5		——[f]	——[f]	——[f]	1668 (s)	1448, 1461 (w) (?)
$[(PhMe_2As)ClPt(OOCCH_3)]_2$	8.35	8.15		24.2	——[h]	10.9	+ 9.0	14.7	1555 (s)	1406 (m)
$[(PhMe_2As)BrPt(OOCCH_3)]_2$	8.16	8.01		23.6	——[h]	17.1	+14.3	14.7	1560 (s)	1408 (m)
$[(PhMe_2As)IPt(OOCCH_3)]_2$	8.09	8.05		24.0	2.4	27.3[i]	+ 6.7	14.1	1557 (s)	1409 (m)
$[(PhMe_2P)_2Cl_2Pt_2OOC(CH_2)_8COO]$	8.16	——[g]	12.7	34.0	——	13.7	+36.6	16.0	1562 (s)	1410 (s)

[a] $CHCl_3$ was columned through alumina to remove EtOH. [b] $\Delta\nu_0$ (cps) is the separation of the $PhMe_2E$ methyl proton resonance signals in the region of no exchange; T_c (°C) is the coalescence temperature; $\Delta G^{\ddagger}_{T_c}$ (kcal/mol) is the free energy of activation. [c] 100-MHz spectrum. [d] 100-MHz spectrum in $CHBr_3$; temperature calibration with ethylene glycol. This complex does not undergo rapid exchange in $HCCl_3$ solution. [e] $J_{^{195}Pt-H}$ for $PhMe_2P$ methyl protons is temperature dependent (see text). [f] Although $\Delta\nu_0$ cps) could not be obtained accurately, since the exchange is not frozen out at −60°, $\Delta G^{\ddagger}_{T_c}$ is estimated to be *ca.* 11 kcal/mol. [g] The protons in the dicarboxylate bridge give rise to a complex temperature-dependent spectrum. [h] $J_{^{195}Pt-H}$ for the carboxylate bridge protons is not clearly resolved. [i] $\Delta\nu_0$ (cps) has been obtained by extrapolation of a plot of $\Delta\nu$ against temperature (see the discussion of activation energies).

methylphenylphosphine)dipalladium(II) (0.32 g) in methylene chloride (10 ml) under a flow of nitrogen. The solution was passed through an alumina column to remove acetic acid and elemental palladium and then evaporated to an orange oil under a flow of nitrogen. Petroleum ether (bp 30–60°) was added to the flask which was stored at 0° for 3 weeks. A yellow solid, which decomposed readily under vacuum, was isolated in poor yield—less than 10%; mp 164–169°. *Anal.* Calcd for $C_{30}H_{38}Cl_2N_6P_2Pd_2$: C, 43.52; H, 4.59. Found: C, 44.19; H, 5.13.

Physical Measurements.—Melting points were recorded on a Kofler hot-stage apparatus and are corrected. Molecular weights were determined osmometrically at 37° using a Mechrolab 301A osmometer. The ^1H nmr spectra were recorded on Varian A56/60D and HA-100 spectrometers. Temperatures of individual spectra were calibrated from a plot[6] of methanol chemical shift against temperature. Unless otherwise specified, the solvent used was ACS spectral analyzed chloroform which has been passed through a column of alumina to remove ethanol. Infrared spectra were recorded as Nujol mulls on a Beckman IR-20 spectrophotometer.

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Results and Discussion

Structural Characterization.—Osmometric determinations of the molecular weights of compounds of general formula $[(Me_2PhE)XM(OOCR)]_2$ showed them to be dimeric in chloroform solution at 37°. The infrared data for the asymmetric and symmetric carboxylate C–O stretching frequencies are tabulated in Table I

and correspond well with previously reported values for bridged carboxylate complexes.[7-10] No absorptions attributable to unidentate carboxylate ligands were observed.

The low-temperature ^1H nmr spectra of the complexes $[(Me_2PhE)XM(OOCR)]_2$ contain two methyl resonances of equal intensity assignable to nonequivalent methyl protons of the Me_2PhE ligand (methyl resonances are singlets for E = As and doublets for E = P; see Table I). The presence at low temperatures of only one resonance signal assignable to the carboxylate bridging ligand (*e.g.*, acetate protons) suggests that the molecular structure of these dimers contains equivalent carboxylate groups—*i.e.*, structure I in which one oxygen of each carboxylate bridge is trans to a halogen and the other is trans to Me_2PhE (a trans arrangement of Me_2PhE ligands).

A conformational isomer with the Me_2PhE groups on different palladium atoms having a cis orientation relative to one another would have two types of carboxylate ligand: one trans to two halogens and one trans to two Me_2PhE ligands. Such a conformational isomer might reasonably be expected to exhibit two bridging carboxylate proton resonances and four carboxylate C–O stretching frequencies in the infrared spectrum (not observed).

Molecular Structure of $[(Me_2PhP)ClPd(OOCCH_3)]_2$.[11] —Preliminary data from X-ray diffraction studies have shown this complex to have a type I molecular structure as shown in Figure 1. The two palladium–

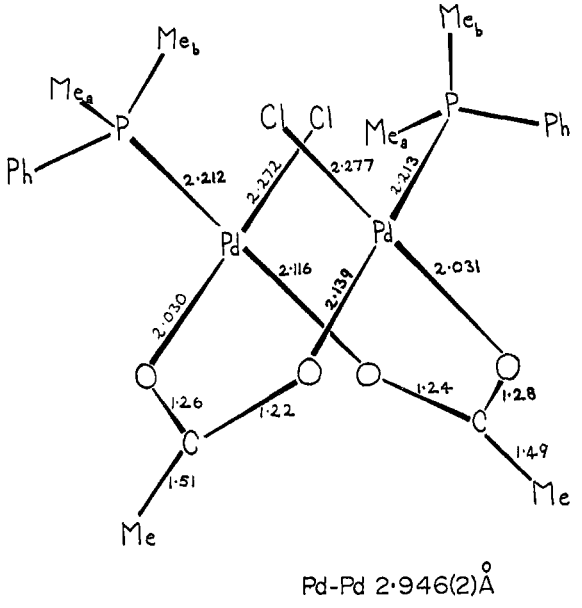

Figure 1.—Molecular structure of $[(Me_2PhP)ClPdOOCCH_3]_2$.[11]

oxygen bonds trans to PMe_2Ph are significantly longer than the palladium–oxgyen bonds trans to Cl as is to be expected from previous studies of relative trans bond weakening effects ($PMe_2Ph \gg Cl$).[12] Asymmetry in the acetate bridges is also observed in the carbon–oxygen distances, the shorter carbon–oxygen bond being trans to PMe_2Ph. This suggests that the trans bond weakening of one of the oxygen–palladium bonds relative to the other is accompanied by some localization of the bonding in the carboxylate unit.

The palladium–palladium distance, 2.946 (2) Å, is in close agreement with the value found for π-allylpalladium acetate dimer,[13] 2.94 (3) Å, and considerably longer than that of elemental palladium, 2.751 Å. In view of the formation of the trimeric complexes $[Pd(OOCCH_3)_2]_3$[14] and $[Pd(OOCCH_3)(ONCMe_2)]_3$[15] with palladium–palladium distances 3.00–3.20 Å and the observation that palladium acetate is monomeric in boiling benzene and trimeric in freezing chloroform, it is unlikely that any appreciable palladium–palladium bonding interaction is occurring in these molecules and that the palladium–palladium distances are a reflection of ligand interactions and bonding requirements.

A chloride atom in $[(Me_2PhP)ClPd(OOCCH_3)]_2$ is at a distance of 2.66 Å from the closest methyl proton of the Me_2PhP unit bonded to the same palladium atom and 2.86 Å from the closest methyl proton of the Me_2PhP bonded to the adjacent palladium atom. The Me_2PhP and Cl ligands on each palladium atom are distorted out of a truly planar coordination and away from the ligands on the adjacent palladium such that the trans O–Pd–Cl angle is *ca.* 171° and the trans O–Pd–P angle is *ca.* 176°. These measurements suggest that significant steric crowding may be anticipated in the complexes with the larger iodo and/or arsine ligands.

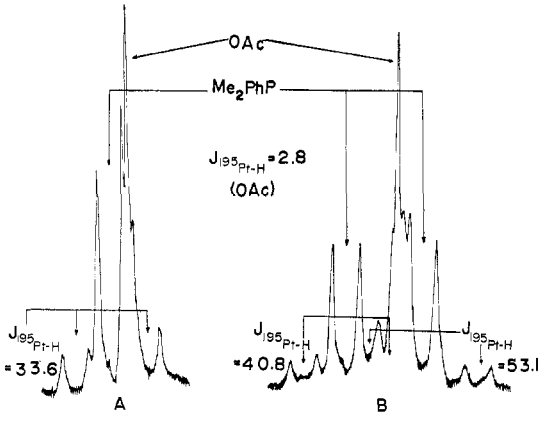

Figure 2.—Methyl proton nmr spectra of a $CHCl_3$ solution of $[(Me_2PhP)IPtOOCCH_3]_2$: (A) in the region of fast exchange, +45°; (B) in the region of no exchange, −20°.

Variable-Temperature ^1H Nmr Studies.—The low-temperature ^1H nmr spectra of the complexes $[(Me_2PhE)XM(OOCR)]_2$ displayed two methyl proton resonances assignable to the nonequivalent methyl groups in I (Table I). [*E.g.*, in Figure 1 methyl groups a and b are nonequivalent owing to the lack of a plane of symmetry in the P–Pd axis. The methyl groups of the two PMe_2Ph ligands are related by a twofold axis of molecular symmetry.] On warming, the two methyl resonances collapse to give a single methyl resonance. For the platinum complexes ^{195}Pt–H coupling with the methyl protons of the EMe_2Ph proton ligand (*ca.* 34

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(14) A. C. Skapski and M. L. Smart, *Chem. Commun.*, 658 (1970).
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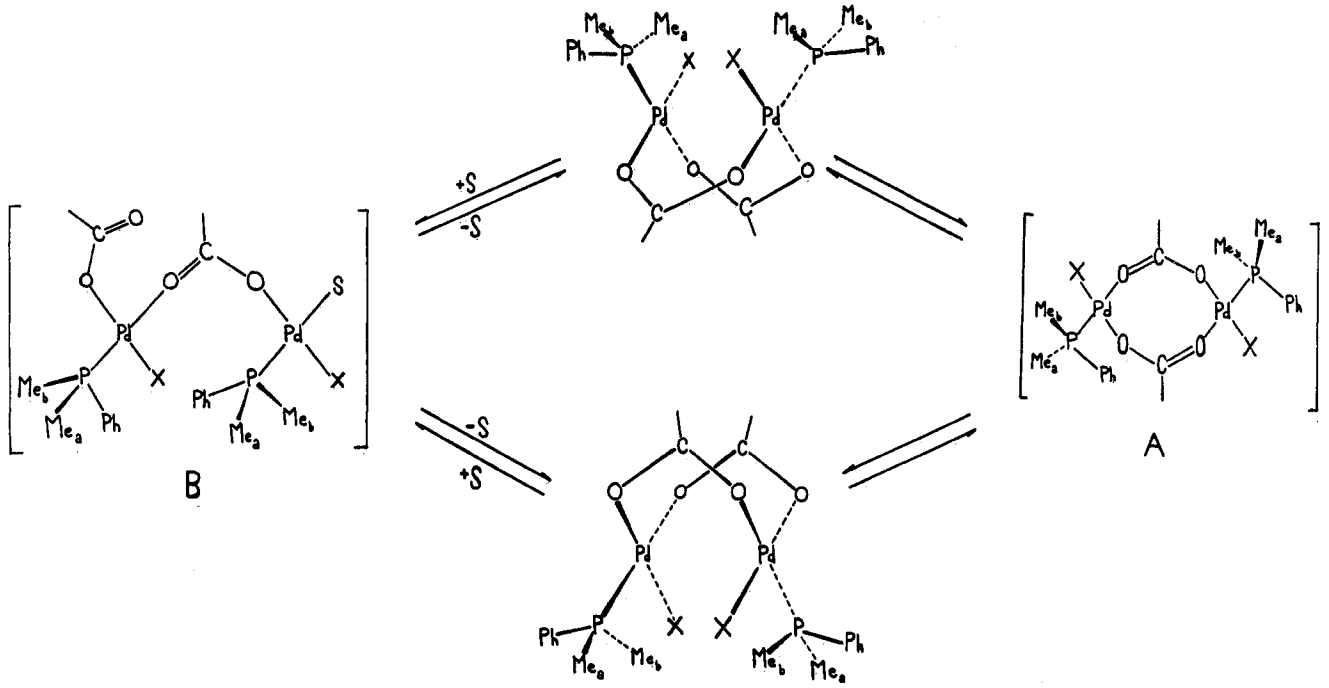


Figure 3.—Proposed mechanisms for methyl proton environment exchange.

cps) and with the carboxylate bridge protons (2.8 cps) is still observed at high temperatures in the region of the fast methyl exchange (Figure 2A). This indicates that the exchange of methyl environments in the platinum complexes cannot involve Me_2PhE dissociation nor carboxylate exchange. While ^{195}Pt–H coupling with bridging acetate protons is temperature invariant, ^{195}Pt–H coupling with the "Me_2PhP methyl protons" in $[(Me_2PhP)IPt(OOCCH_3)]_2$ exhibits an unusual temperature dependence. At −20°, the high-field methyl resonance has a $J_{^{195}Pt-H}$ value of 53.1 cps and the low-field methyl resonance has $J_{^{195}Pt-H}$ = 40.8 cps (Figure 2B). In the region of fast exchange $J_{^{195}Pt-H}$ = 33.6 cps which is comparable to the value found for the bridging halide dimers $[(Me_2PhP)PtX_2]_2$.[4] The larger magnitude of $J_{^{195}Pt-H}$ at low temperatures suggests restricted rotation about the Pt–P bond and that the different coupling constants arise out of a specific orientation of the Me_2PhP ligands in the molecule. On warming, the ^{195}Pt satellite peaks collapse prior to collapse of the main peaks suggesting that rapid rotation about the P–Pt axis is occurring resulting in a change in ^{195}Pt coupling. For the corresponding chloro and bromo complexes ^{195}Pt–Me_2PhP coupling was not resolved even at −60°. At high temperatures the observed ^{195}Pt–Me_2PhP coupling constant is the average of all possible orientations. Hindered rotation about the P–Pt axis in $[(Me_2PhP)IPt(OOCCH_3)]_2$ is not surprising in view of the fairly crowded structure observed for $[(Me_2PhP)ClPd(OOCCH_3)]_2$ (Figure 1).

The various possible mechanisms which would lead to exchange of the nonequivalent methyl proton environments in the complexes of type I may be categorized as follows: (*1*) associative—probably bimolecular in complex; (2) dissociative—either *via* bridge breaking to give a monomeric intermediate $[(Me_2PhE)XM(OOCR)]$ or *via* halide and/or Me_2PhE dissociation; (3) nondissociative—either a rearrangement of ligands *via* a halide-bridged dimeric intermediate or an inversion of the boat conformation of the $M_2(OCO)_2$ ring in I (see Figure 3, route A) as previously proposed for $[(\pi\text{-allyl})Pd(OOCCH_3)]_2$;[1,2] (4) partially dissociative—solvolytic cleavage of *one* metal–oxygen bond followed by a rearrangement of the monocarboxylate-bridged intermediate and re-formation of the metal–oxygen bond (Figure 3, route B) [^{195}Pt coupling with the carboxylate bridge and Me_2PhE protons in the region of fast exchange (see Table I) eliminates the carboxylate and Me_2PhE dissociative processes in the case of the platinum complexes].

At 37° in $CHCl_3$, the Me_2PhAs methyl proton and the $OOCCH_2Cl$ methylene proton resonances of both $[(Me_2PhAs)ClPd(OOCCH_2Cl)]_2$ and $[(Me_2PhAs)IPd(OOCCH_2Cl)]_2$ consist of sharp singlets (*i.e.*, the exchange of methyl environments is rapid at this temperature). A 5:1 chloride–iodide mixture of these complexes in $CHCl_3$ at 37° gave four Me_2PhAs methyl proton resonances and four chlorocarboxylate methylene proton resonances as shown in Figure 4. The high-field methyl and methylene proton resonances of greatest intensity may be assigned to the chloro complex and the low-field resonances of lowest intensity may be assigned to the iodo complex. The two intermediate resonances of equal intensity may be assigned to the mixed chloro–iodo complex. In the region of fast-exchange resonances assignable to both, the mixed-ligand species and the original complexes were also observed for the following mixtures: $[(Me_2PhP)ClPd(OOCCMe_3)]_2$ and $[(Me_2PhP)IPd(OOCCMe_3)]_2$, $[(Me_2PhP)ClPt(OOCCMe_3)]_2$ and $[(Me_2PhP)IPt(OOCCMe_3)]_2$, $[(Me_2PhP)ClPd(OOCCH_2Cl)]_2$ and $[(Me_2PhAs)ClPd(OOCCH_2Cl)]_2$, and $[(Me_2PhP)ClPd(OOCCMe_3)]_2$ and $[(Me_2PhP)ClPd(OOCCH_2Br)]_2$. The absence of rapid exchange (on the ^1H nmr time scale) of halide, Me_2PhE, or carboxylate ligand at temperatures where Me_2PhE methyl groups are equivalent precludes the operation of the associative and dissociative mechanisms (mechanisms 1 and 2) and

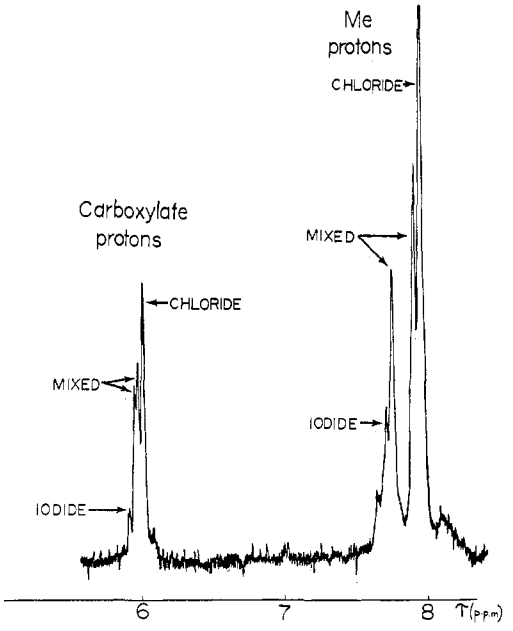


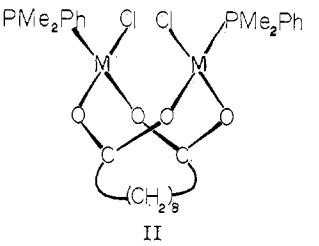
Figure 4.—The ^1H nmr of a 1:5 mixture of $[(Me_2PhAs)IPd\text{-}OOCCH_2Cl]_2$ and $[(Me_2PhAs)ClPdOOCCH_2Cl]_2$ in chloroform at 37°.

also a nondissociative mechanism *via* a halide-bridged intermediate. (N.B. Two Me_2PhE methyl resonances were observed for mixed chloro–iodo species.)

At the temperature of coalescence of Me_2PhE methyl protons in complexes of type I the rate of exchange is concentration *independent* over a threefold dilution range which is consistent with an intramolecular inversion of the carboxylate bridges *via* a nondissociative or partially dissociative mechanism as shown in Figure 3. In order to distinguish between the two possibilities a series of μ-dicarboxylate complexes of the type $[(Me_2PhP)_2Cl_2M_2OOC(CH_2)_nCOO]_x$ (M = Pd, Pt; n = 3–8) were prepared. The solubility and molecular weights of these complexes in chloroform solution at 37° are tabulated in Table II. For the sebacate complexes (n = 8) molecular weight studies and the asymmetric and symmetric C–O stretching frequencies (Table I) are consistent with the bridging carboxylate structure II. For values of n less than 8 (sebacate, x = 1) the observed molecular weight is greater than that calculated for a dinuclear molecule. Molecular

TABLE II
MOLECULAR WEIGHTS IN $CHCl_3$ AT 37°

	Solubility	Exptl mol wt	Mol wt of dinuclear complex (x = 1)
	$[(Me_2PhP)_2Cl_2M_2OOC(CH_2)_nCOO]_x$		
M = Pd, n = 3	Insoluble	...	...
n = 4	Sparingly soluble	1190 ± 290	704.1
n = 6	Slightly soluble	955 ± 57	732.2
n = 7	Soluble	892 ± 20	746.2
n = 8	Soluble	766 ± 20	760.2
M = Pt, n = 8	Soluble	950 ± 20	937.3
	$[(\pi\text{-allyl})_2Pd_2OOC(CH_2)_nCOO]_x$		
n = 7	Soluble	719 ± 20	480.4
n = 8	Soluble	645 ± 20	494.4



II

models suggest that the dicarboxylate must have a methylene chain of *at least* six for a dinuclear μ-dicarboxylate species to exist without unreasonable steric strain. Molecular weights and solubilities for n = 3 and 4 indicate polymeric structures for these compounds (Table II).

The methylene linkages between the carboxylate bridges in molecules of type II should prevent a nondissociative inversion of the $M_2(OCO)_2$ ring system. The nmr spectrum of a saturated $CHCl_3$ solution of the sebacate complex $[(Me_2PhP)_2Cl_2Pd_2OOC(CH_2)_8COO]$ at −20° contains two overlapping doublets in the methyl region assignable to Me_2PhP methyl protons—$J_{^{31}P-H}$ = 13.0 cps and separation between doublets $\Delta\nu$ = 13.1 cps (see Figure 5). The corresponding

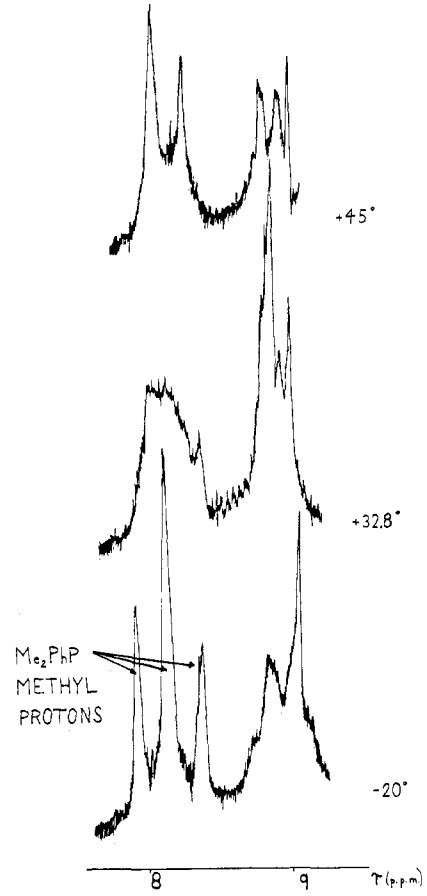


Figure 5.—Temperature-dependent methyl proton nmr spectra of $[(Me_2PhP)_2Cl_2Pd_2OOC(CH_2)_8COO]$.

azelate (n = 7) gave a similar low-temperature spectrum ($J_{^{31}P-H}$ = 13.9 cps and $\Delta\nu$ = 14.2 cps) as did the analogous platinum sebacate complex ($J_{^{31}P-H}$ = 12.7 cps and $\Delta\nu$ = 13.7 cps). The Me_2PhP methyl proton resonances overlap the terminal methylene proton resonances of the μ-dicarboxylate ligand. The other

dicarboxylate methylene protons give rise to a complex nmr pattern in the region τ 7.6–9.4 ppm. On warming solutions of the sebacate and azelate complexes to +40° the methyl resonances coalesce to a single doublet resonance. The nmr spectra of the dicarboxylate methylene protons, though complex, are also temperature dependent between −20 and +40°. At the coalescence temperature for $[(Me_2PhP)_2Cl_2Pd_2OOC(CH_2)_8COO]$ the rate of methyl exchange is independent of concentration over a twofold dilution. In the analogous platinum sebacate complex ^{195}Pt–Me_2PhP coupling is still observed in the region of fast exchange. Of the two possible mechanisms for methyl exchange outlined in Figure 3, only the solvent-assisted partially dissociative process is possible for μ-dicarboxylate complexes of type II.

Addition of Weak Bridge-Splitting Ligands.—Addition of small aliquots of methanol to $CHCl_3$ solutions of complexes of types I and II at temperatures just below the Me_2PhE methyl coalescence temperature effects a considerable increase in the rate of exchange (*e.g.*, see Figure 6) without affecting the nmr spectra

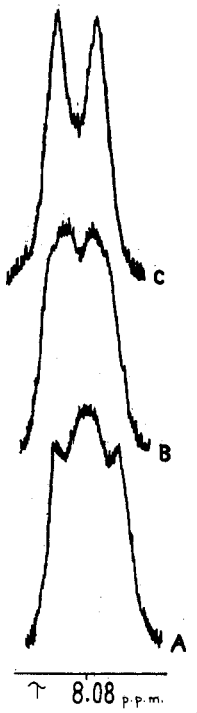


Figure 6.—Methyl proton nmr of a $CHCl_3$ solution of $[(Me_2PhP)ClPdOOCCH_2Br]_2$ at −12° (A), after addition of one methanol per palladium (B), and after addition of five methanols per palladium (C).

of the complexes at low temperatures in the absence of exchange. Similarly addition of acetic acid to $CHCl_3$ solutions of $[(Me_2PhP)BrPt(OOCH_2Cl)]_2$ ($CH_3COOH:Pt \approx 1$) also lowers the coalescence temperature without affecting the low-temperature nmr spectrum of the complex. The chemical shifts of the acetic acid protons are unchanged from those of an identical concentration of acetic acid in chloroform without complex present. No bridging acetate species is observed even at a $CH_3COOH:Pt$ ratio of 2. The observation of separate unshifted singlet resonances assignable to free acid and carboxylate bridge when one monochloroacetic acid molecule per platinum atom is added to a $CHCl_3$ solution of $[(Me_2PhP)BrPt(OOCCH_2Cl)]_2$ at 46° (fast methyl exchange) eliminates the possibility of rapid free acid–bridging carboxylate exchange. Such addition does however markedly enhance the rate of methyl exchange. The above observations of rate enhancement by methanol and carboxylic acids indicate that the methyl exchange process is extremely sensitive to the nature of the solvent present as would be expected for a solvent-assisted partially dissociative mechanism.

Addition of small aliquots of acetone to $CHCl_3$ solutions of complexes of types I and II has no effect on the rate of exchange and it would appear that acetone does not effectively compete with chloroform in the solvolysis of the metal–oxygen bond. This order of solvating ability concurs with that previously noted for platinum(II) substitution reactions.[16]

Addition of a strongly coordinating ligand such as pyridine to a $CHCl_3$ solution of $[(Me_2PhP)BrPd(OOCCMe_3)]_2$ at −54° at a py:Pd ratio of 1 results in a bridge-splitting reaction and the nmr spectrum contains a doublet at τ 8.24 (Me_2PhP, J_{P-H} = 12.9 cps) and a singlet at τ 9.19 assignable to the solution species $[(Me_2PhP)BrPd(OOCCMe_3)py]$. On warming this solution to room temperature at least three new doublet resonances assignable to coordinated Me_2PhP ligands appear and presumably the initially formed monomer is undergoing disproportionation (ligand exchange, etc.).

Free Energies of Activation, $\Delta G^{\ddagger}_{T_c}$. The separation of the nonequivalent methyl proton resonances in complexes of type I in the absence of exchange, $\Delta\nu_0$, and the coalescence temperatures of the methyl proton resonances, T_c (see Table I), may be substituted into the Gutowsky–Holm expression (eq 1) for the rate of exchange, k.[17] Substitution of k into the derived Eyring equation (eq 2) gives the free energy of activation,

$$k = \frac{\pi}{\sqrt{2}}\Delta\nu_0 \qquad (1)$$

$$\Delta G^{\ddagger}_{T_c} = 4.576T_c[10.319 + \log(T_c/k)] \qquad (2)$$

$\Delta G^{\ddagger}_{T_c}$ (Table I). The dimethylphenylarsine complexes fulfill all the conditions of the Gutowsky–Holm treatment[17] since the exchange is between the uncoupled sites of equal population, the lifetimes in each site are equal, the midpoint of the resonance pattern is temperature invariant, and $\Delta\nu_0$ is large. The extension of these expressions to the phosphine complexes in which there is coupling seems justified since J_{PH} is large and independent of temperature and also because the $\Delta G^{\ddagger}_{T_c}$ values obtained are in excellent agreement with those of the arsine analogs.

For the complexes $[(Me_2PhE)XM(OOCR)]_2$ of type I the free energy of activation $\Delta G^{\ddagger}_{T_c}$ of the partially dissociative bridge-inversion process is markedly dependent on the nature of the bridging carboxylate ligand. For a series of analogous complexes $\Delta\nu_0$ shows little variation, T_c tends to decrease, and $\Delta G^{\ddagger}_{T_c}$ decreases with increasing electronegative substituents on the α carbon of the carboxylate ligand and correlates reasonably well with the pK_a of the corresponding

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(17) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

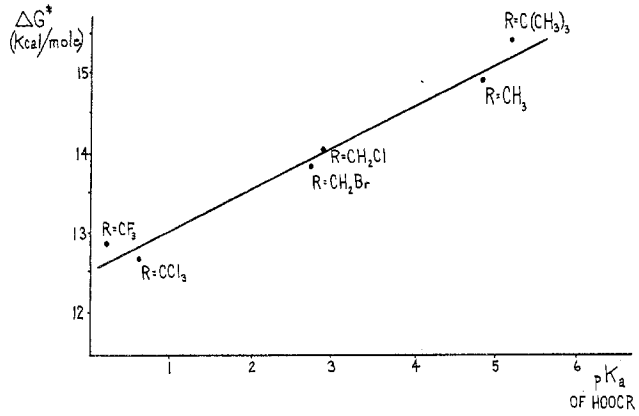

Figure 7.—Correlation of free energy of activation with pK_a of the carboxylic acid, HOOCR, for the process of methyl environment exchange in $[(Me_2PhP)ClPdOOCR]_2$.

carboxylic acid (Figure 7). Electron withdrawing substituents on the α carbon would be expected to stabilize the unidentate carboxylate intermediate (Figure 3, route B) in the proposed partially dissociative mechanism. The exceptionally high free energy of activation for the bridging triphenylacetate complex $[(Me_2PhP)ClPd(OOCCPh_3)]_2$ (T_c(in $CHBr_3$) = +83°; $\Delta G^{\ddagger}_{T_c}$ = 17.2 kcal/mol) may reflect destabilization of the mono-unidentate carboxylate intermediate (Figure 3, route B) due to steric factors associated with the bulky triphenylacetate ligand.

The variation of $\Delta G^{\ddagger}_{T_c}$ as a function of the halide ligand is shown in Table III. The observed trends are

TABLE III
VARIATION OF $\Delta G^{\ddagger}_{T_c}$ WITH HALIDE X

Complex	Order of increasing $\Delta G^{\ddagger}_{T_c}$
$[(Me_2PhP)XPt(OOCR)]_2$	Cl < I < Br
$[(Me_2PhP)XPd(OOCR)]_2$	I < Cl < Br
$[(Me_2PhAs)XPt(OOCR)]_2$	I < Cl ≈ Br
$[(Me_2PhAs)XPd(OOCR)]_2$	I ≈ Br < Cl

independent of the nature of the carboxylate bridge but dependent on the metal and the Me_2PhE ligand. The observed trends may be rationalized in terms of competing electronic and steric effects, the steric effects predominating with the bulkier ligands (I, Me_2PhAs). On the basis of the molecular structure of $[(Me_2PhP)ClPd(OOCCH_3)]_2$ and the observation in $[(Me_2PhP)IPt(OOCCH_3)]_2$ of restricted rotation at the P–Pt bond considerable steric crowding in iodide and to a lesser extent in Me_2PhAs complexes of type I may be expected to increase the free energy of the boat configuration I and hence lower the free energy of activation, $\Delta G^{\ddagger}_{T_c}$. Steric effects are more predominant for the palladium complexes than for the platinum complexes or alternatively (and more probable) electronic effects are more predominant for the platinum complexes. Thus in the dimethylphenylphosphinepalladium and -platinum carboxylate complexes, $\Delta G^{\ddagger}_{T_c}$ for both the iodide and bromide is less than that of the chloride. In the arsine analogs the steric effect is more important and $\Delta G^{\ddagger}_{T_c}$ decreases with the increase in the size of the halide.

Activation Energy.—Approximate values for the activation energy of the exchange process have been obtained graphically from plots of the Arrhenius equation (Figure 8), the rate of exchange, k, being determined by variable-temperature ^1H nmr data in the region of slow exchange by the method of peak separation[17,18]

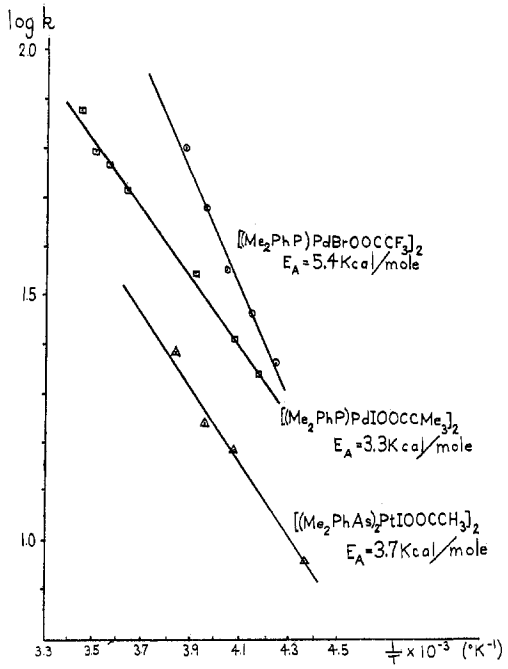

Figure 8.—Activation energies for methyl proton environment exchange.

$$k = \frac{1}{2\tau} = \frac{\pi}{\sqrt{2}}((\Delta\nu_0)^2 - (\Delta\nu)^2)^{1/2} \qquad (3)$$

The conditions of applicability of eq 3 are identical with those of eq 1 which has been previously discussed for type I complexes. $\Delta\nu_0$ has been obtained by extrapolation due to the onset of other processes before the no-exchange limit has been achieved, as such values of E_a in Figure 8 can only be considered to be approximate (±3.0 kcal/mol). However the calculated activation energies, E_a, of the methyl site exchange processes for complexes of type I are much lower than $\Delta G^{\ddagger}_{T_c}$ and in the range 3–6 kcal/mol (see Figure 8). Since E_a and the enthalpy of activation $\Delta H^{\ddagger}$ are of similar magnitudes, this difference must be attributed to a large negative value for the entropy of activation $\Delta S^{\ddagger}_{T_c}$ (−20 to −40 eu) as would be expected for a solvent-assisted process[19] such as that illustrated in Figure 3, route B. Entropies of activation for ring inversion in six-, seven-, and eight-membered cyclic organic molecules have been generally observed by nmr spectroscopy to be in the range +10 to −10 eu.[20-28] It should be realized however that a $M_2C_2O_4$ "ring inversion" mechanism (Figure 3, route A), which had to pass through a sterically and electronically restricted transition state, might also be expected to give rise to large negative entropies of activation.[23,24] However the marked similarity be-

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tween the behavior of the di-μ-carboxylate complexes and the dinuclear sebacate complexes eliminates this latter possibility.

The discontinuity in the behavior of $\Delta\nu$ at low temperatures (Figure 9) may well be due to freezing out of

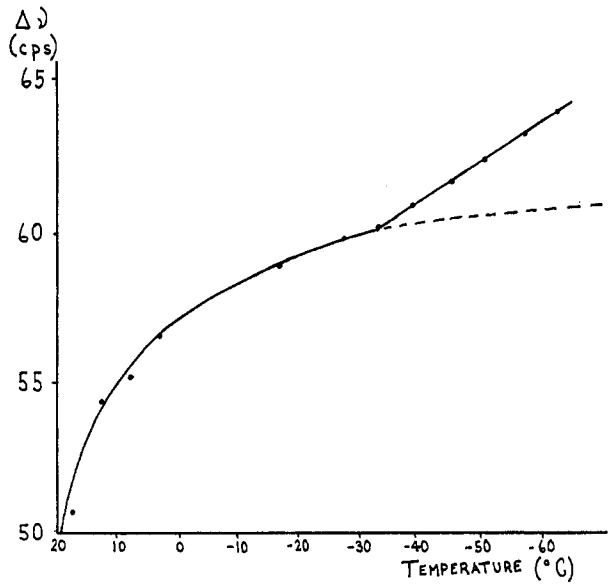

Figure 9.—Variation of peak separation, $\Delta\nu$ (cps), with temperature (°C) for $[(Me_2PhP)IPdOOCCMe_3]_2$. A $\Delta\nu_0$ of 61.0 cps has been obtained by extrapolation.

specific orientations of the phosphine as observed in the hindered rotation of Me_2PhP about the P–Pt axis in $[(Me_2PhP)IPt(OOCCH_3)]_2$ (Figure 2) and/or viscosity effects. The half-height line width of the methyl proton resonances increased with decreasing temperature below −20°.

An unusual feature of the solvolytic cleavage of the metal–carboxylate bond is that the rate and thermodynamic activation parameters for analogous palladium and platinum complexes are similar (*e.g.*, the pseudo-first-order rate constant k (eq 1) for $[Br(Me_2PhP)Pd(OOCCH_3)]_2$ at 27.5° is 52.9 sec^{-1} and for $[Br(Me_2PhP)Pt(OOCCH_3)]_2$ at 29.5° is 52.2 sec^{-1}. In general the rate of ligand substitution at platinum(II) is usually several orders of magnitude slower than at palladium(II).[25] However very little quantitative kinetic data have been obtained for bridge-cleavage reactions. Studies of the substitution of bridge halide complexes of platinum(II) have shown the rate of substitution to be two to three orders of magnitude faster than for corresponding monomeric complexes.[26] In the solvolytic cleavage of a metal-bridging carboxylate bond in complexes of type I the breaking of one M–O bond would reduce the steric strain within the molecule. A simultaneous strengthening of the other M–O bond on formation of the unidentate carboxylate intermediate (Figure 3, route B) would be anticipated to accompany the relief of strain in that M–O bond and as such the activation energy might be expected to be low and not as markedly dependent on M. Furthermore the predominant factor in $\Delta G^{\ddagger}$ for the exchange process is the entropy of activation which would also lead to a smaller difference in the relative rates of palladium(II) and platinum(II) analogs.

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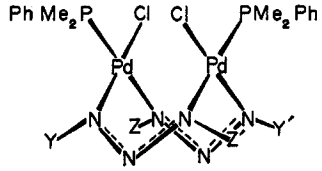
Bridging *cis*-Di-μ-triazenido Complexes of Palladium(II).—Addition of diazoaminobenzene to $[Cl(Me_2PhP)Pd(OOCCH_3)]_2$ results in displacement of acetic acid and formation of the bridging 1,3-diphenyltriazenido complex $[Cl(Me_2PhP)Pd(PhNNNPh)]_2$. The ^1H nmr spectrum (Table IV) of this complex contains two doublets of equal intensity assignable to nonequivalent Me_2PhP methyl protons consistent with a bridged triazenido structure stereochemically analogous to complexes of type I. At 50° in $CHCl_3$ no exchange of methyl proton environments was observed in the nmr spectrum which is consistent with previous studies of π-allylic palladium μ-triazenide dimers.[3] The more complex nmr spectrum obtained for $[Cl(Me_2PhP)Pd(MeNNNPh)]_2$ (Table IV) contains four doublets of

TABLE IV
^1H NMR DATA FOR BRIDGING TRIAZENIDO COMPLEXES OF PALLADIUM(II) RECORDED IN $CHCl_3$ SOLUTION

	Methyl proton resonances		$J^{31}P-H$, cps	
Complex	Me_2PhP	MeN-NNPh	Me_2PhP	MeN-NNPh
$[Cl(Me_2PhP)Pd(PhNNNPh)]_2$[a]	8.30	...	12.4	...
	8.65	...	12.4	...
$[Cl(Me_2PhP)Pd(MeNNNPh)]_2$[b]	8.40	8.33	13.0	...
	8.22	6.24[c]	13.0	1.9
	8.05	...	13.0	...
	8.01	...	13.0	...

[a] At 60 MHz. [b] At 100 MHz. [c] Trans to Me_2PhP.

equal intensity assignable to two stereochemically distinct Me_2PhP ligands each with nonequivalent methyl groups. The methyl protons of the MeNNNPh ligands give rise to a singlet resonance at τ 8.33 assigned to the methyl group trans to Cl and a doublet resonance of equal intensity at τ 6.24 assigned to the methyl group trans to PMe_2Ph [$J_{P-Pd-N-C-H}$ = 1.9 cps]. The downfield shift of 2.09 ppm is probably due to the large trans bond weakening effect of Me_2PhP relative to Cl resulting in localization of the triazenido bonding at the methyl nitrogen. The nmr spectrum of $[Cl(Me_2PhP)Pd(MeNNNPh)]_2$ may be interpreted in terms of either a 1:1 mixture of IIIa and IIIb or isomer IV



IIIa, Y = Y′ = Me; Z = Z′ = Ph
IIIb, Y = Y′ = Ph; Z = Z′ = Me
IV, Y = Z = Ph; Y′ = Z′ = Me

alone. The absence of a rapid exchange of methyl groups in the triazenido complexes similar to the partially dissociative mechanism of methyl exchange observed in the analogous bridging carboxylates is probably due to the relative nonlability of the palladium–nitrogen bond relative to the palladium–oxygen bond.[27]

A Reinvestigation of π-Allylic Palladium Carboxylate Dimers.—Addition of small aliquots of methanol, acetic acid, or dimethyl sulfoxide[1] to chloroform solutions of π-allylpalladium acetate dimer increases the rate of exchange of the nonidentical π-allylic groups in the nonsymmetrical conformational isomer and de-

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creases the coalescence temperature, while leaving the low-temperature spectrum in the absence of exchange unaffected. Addition of small aliquots of acetone has no effect on the coalescence temperature. This behavior is identical with the effect of these solvents on the exchange of methyl environments in bridged carboxylate complexes of type I. Furthermore the palladium–oxygen bond length in π-allylpalladium acetate dimer is similar to that trans to Me_2PhP in $[Cl(Me_2PhP)Pd(OOCCH_3)]_2$ (2.11 ± 0.02 and 2.13 ± 0.02 Å, respectively).[13] As such it is probable that exchange of the nonidentical allyl groups in the nonsymmetrical conformer of π-allylpalladium acetate also occurs *via* a partially dissociative mechanism and not *via* the previously proposed inversion of the $Pd_2C_2O_4$ ring.

In the complexes $[(\pi\text{-allyl})_2Pd_2[OOC(CH_2)_nCOO]]$ (n = 7, 8), the absence of exchange on the nmr time scale of the nonidentical allyl groups of the nonsymmetrical isomer prior to intermolecular exchange of allyl groups between isomers has been taken by van Leeuwen and Praat[2] to indicate that the apparent "intramolecular exchange process occurring in the nonsymmetrical isomer of allylpalladium acetate does not occur in the corresponding azelate and sebacate complexes." We have found these complexes to be partially polymeric and/or tetrameric in solution (Table II) and to give temperature-dependent nmr spectra which are too complex to interpret mechanistically.

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Reactions of Tris(triphenylphosphine)platinum(0). I. The Preparation and Properties of Bis(triphenylphosphine)platinum(0)–Silicon Tetrafluoride[1a]

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Treatment of tris(triphenylphosphine)platinum(0) with silicon tetrafluoride affords the Lewis salt bis(triphenylphosphine)-platinum(0)–silicon tetrafluoride, $[(C_6H_5)_3P]_2Pt\cdot SiF_4$ (I). The reactions of compound I with I_2, HCl, and NH_3 are discussed. The pyrolysis of I is compared to that of $[(C_6H_5)_3P]_3Pt$ with both complexes affording benzene and a nonvolatile platinum species which exhibits an esr signal, g = 2.014. A new SiF_5^- salt, triphenylmethylphosphonium pentafluorosilicate, has been prepared and the chemistry of SiF_5^- salts is discussed and compared to that of I.

Introduction

The preparation and characterization of the Lewis acid–base adduct, $[(C_6H_5)_3P]_2Pt\cdot SiF_4$, is described herein while adducts with BCl_3 are reported elsewhere.[2] The isolated Lewis acid complexes of platinum may be viewed as model compounds for intermediates probably formed during the general reaction referred to as oxidative addition.

Results and Discussion

Preparation and Purification of $[(C_6H_5)_3P]_2Pt\cdot SiF_4$.—Treatment of $[(C_6H_5)_3P]_3Pt$, dissolved in benzene, with SiF_4 at room temperature affords a finely divided off-white crystalline precipitate, $[(C_6H_5)_3P]_2Pt\cdot SiF_4$ (I). The mole ratio of platinum complex to silicon halide is 1:1 within 3 mol %. After filtration, $P(C_6H_5)_3$ can be isolated from the filtrate in *ca.* 1:1 mole ratio with the starting platinum complex. This chemical transformation is summarized by eq 1. Halpern has demon-

$$[(C_6H_5)_3P]_3Pt + SiF_4 \longrightarrow [(C_6H_5)_3P]_2Pt\cdot SiF_4 + P(C_6H_5)_3 \quad (1)$$

strated that $[(C_6H_5)_3P]_3Pt$ dissociates in benzene to the reactive intermediate $\{[(C_6H_5)_3P]_2Pt\}$ and free triphenylphosphine.[3] The "bis" adduct of platinum is probably the reactive species in the reaction with SiF_4; therefore as the reaction proceeds, eq 1, the concentration of free $P(C_6H_5)_3$ increases which results in a decreased concentration of the "bis" adduct thereby decreasing the rate of formation of I. The consistency of this postulate is inferred from the data summarized in Table I.

Infrared Studies.—The infrared spectrum of I, Figure 1 and Table II, has absorptions at 875, 780, 477, and 443 cm^{-1} which are assigned to SiF vibrations. The remaining absorptions can be assigned to coordinated $P(C_6H_5)_3$ ligand vibrations. The infrared spectra of complexed $P(C_6H_5)_3$ ligands are practically invariant from 4000 to 250 cm^{-1}. The region from 4000 to 600 cm^{-1} is characteristic of monosubstituted benzene; the absorptions occurring from 600 to 250 cm^{-1} are associated with P–C modes; however, no specific bands can be assigned to P–C stretching vibrations because they are often coupled with ring vibrations. There are several bands, called "X"-sensitive vibrations, which change with the nature of the complex. The most important of these vibrations occurs at 1100 ± 20 cm^{-1}. Kross and Fassel[4] observed that this band shifts to higher energy as the electronegativity of the

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