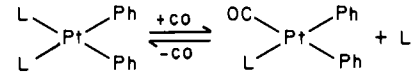
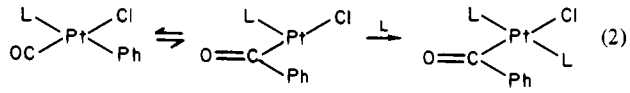
regeneration of the diaryl complex (eq 1).



$$L = PPh_2Me, PPh_3 \qquad (1)$$

The mechanism of carbonyl insertion has been investigated in depth[8,9,23–25] for complexes of the type *trans*-[PtPhClL$_2$] (L = tertiary phosphine, arsine, etc.) and shown to proceed in certain cases via initial phosphine displacement followed by phenyl migration to yield a 14-electron "T-shaped" intermediate. Reaction of the unsaturated intermediate with the displaced phosphine thus yields the product *trans*-[PtCl(COPh)L$_2$] (eq 2). The phenyl migration reaction does not



(2)

occur with the diphenylplatinum complexes; the geometry of the "T-shaped" intermediate formed by such a migration would require the phenyl and benzoyl groups to be mutually trans, a disfavored arrangement of such high trans-influence ligands.[11] The reaction thus proceeds only as far as the *cis*-[PtPh$_2$(PR$_3$)(CO)] complex, and no insertion products are formed. The lack of insertion observed with complexes of bidentate ligands can be attributed to the prevention of the initial step in the insertion process, phosphine displacement by carbon monoxide, because of the chelating ability of these ligands. Interestingly, we have recently observed[18] that platinum(II) complexes of monodentate phosphines show high catalytic activity in the homogeneous hydroformylation of olefins, in which carbonyl insertion is believed to be a fundamental step, compared with the reported activity of platinum(II) complexes of chelating phosphines.[26] All such systems, however, require the use of additives such as tin(II) halides to obtain high activity. A subsequent paper[27] will concern the effects of tin(II) halides on the stoichiometric carbonylation and decarbonylation reactions of platinum(II) phenyl derivatives.

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Registry No. *cis*-[PtCl$_2$(PMePh$_2$)$_2$], 16633-72-0; *trans*-[PtCl$_2$(PCy$_3$)$_2$], 60158-99-8; *trans*-[PtClPh(PMePh$_2$)$_2$], 60772-01-2; *trans*-[PtClPh(PCy$_3$)$_2$], 60750-86-9; *trans*-{PtClPh[P(*o*-tolyl)$_3$]$_2$}, 78064-13-8; *trans*-[PtCl(COPh)(PMePh$_2$)$_2$], 60742-07-6; *trans*-[PtCl(COPh)(PCy$_3$)$_2$], 78064-14-9; *cis*-[PtPh$_2$(PMePh$_2$)$_2$], 51538-76-2; *trans*-[PtCl(COPh)(PPh$_3$)$_2$], 18421-48-2; Pt$_2$(μ-Cl)$_2$Cl$_2$(PCy$_3$)$_2$, 78147-52-1; Pt$_2$(μ-Cl)$_2$Ph$_2$(PCy$_3$)$_2$, 78064-15-0; Pt$_2$(μ-Cl)$_2$Ph$_2$[P(*o*-tolyl)$_3$]$_2$ (*sym* isomer), 78064-16-1; Pt$_2$(μ-Cl)$_2$(COPh)$_2$(PCy$_3$)$_2$, 78147-53-2; PtClPh(CO)(PCy$_3$), 78147-54-3; PtClPh(CO)[P(*o*-tolyl)$_3$], 74139-73-4; *cis*-[PtPh$_2$(CO)(PMePh$_2$)], 78088-86-5; *cis*-[PtPh$_2$(CO)(PPh$_3$)], 78064-17-2; PtCl$_2$(dppm), 52595-94-5; PtCl$_2$(dppe), 14647-25-7; PtCl$_2$(appe), 14647-20-2; PtPh$_2$(dppm), 52621-11-1; PtPh$_2$(dppe), 52595-92-3; PtPh$_2$(appe), 78064-18-3; PtClPh(dppm), 78064-19-4; PtClPh(dppe), 27711-51-9; PtClPh(appe), 78064-12-7; PtCl(COPh)(dppe), 78064-20-7; PtCl(COPh)(appe), 78064-11-6; [Pt$_2$(μ-Cl)(μ-dppm)$_2$(Ph)$_2$]Cl, 78064-21-8; [Pt$_2$(μ-Cl)(μ-dppm)$_2$(COPh)$_2$]Cl, 78064-22-9; PtCl$_2$(cod), 12080-32-9; PtClPh(cod), 51177-65-2; PtCl(COPh)(cod), 76705-02-7; PtPh$_2$(cod), 12277-88-2; PtPh$_2$(PPh$_3$)$_2$, 50988-66-4; PtClPh(PPh$_3$)$_2$, 16744-25-5; Pt$_2$(μ-Cl)$_2$Ph$_2$[P(*o*-tolyl)$_3$]$_2$ (*unsym* isomer), 78147-55-4.

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Preparation, Characterization, and Some Reactions of Tri-*tert*-butylarsine Complexes of Platinum(II) and Palladium(II) Chlorides

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As(*t*-Bu)$_3$ reacts with platinum(II) chlorides to afford either *trans*-PtCl$_2$[As(*t*-Bu)$_3$]$_2$ or the dinuclear complex Pt$_2$(μ-Cl)$_2$Cl$_2$[As(*t*-Bu)$_3$]$_2$. With palladium(II) chloride, however, only the dinuclear complex Pd$_2$(μ-Cl)$_2$Cl$_2$[As(*t*-Bu)$_3$]$_2$ is formed even in the presence of excess As(*t*-Bu)$_3$. These complexes undergo substitution and/or bridge-cleavage reactions with CO, py, AsPh$_3$, Cl$^-$, or tertiary phosphines.

Introduction

It has now been well recognized that the properties of the metal complexes of phosphorus donor ligands[2–4] are markedly affected by the electronic and the steric[4] effects of the substituents on phosphorus. However, investigations on the electronic and/or the steric effects in metal complexes of arsenic or antimony donor ligands[2] have been lacking. As part of a systematic study of the steric effects in platinum metal complexes of tertiary phosphines, arsines, and stibines, platinum and palladium complexes of tri-*tert*-butylphosphine,[5–7] -arsine,[8] and -stibine[9] have been investigated in this laboratory. Recently we reported on the stabilization of platinum(II) and palladium(II) hydride complexes[8] by tri-*tert*-butylarsine. Preparation, characterization, and some reactions of tri-

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Table I. Melting Points and Analytical and Molecular Weight Data of Tri-*tert*-butylarsine Complexes

complex	mp,[a] °C	anal. % calcd C	calcd H	calcd Cl	found C	found H	found Cl	mol wt calcd	mol wt found
trans-$PtCl_2[As(t\text{-}Bu)_3]_2$	170–175 dec	38.00	7.12	9.37	37.88	7.10	9.30	758	747[b]
$\{PtCl_2[As(t\text{-}Bu)_3]\}_2$	175–180 dec	28.13	5.32	13.84	28.22	5.42	13.60	1025	1002[b]
$\{PdCl_2[As(t\text{-}Bu)_3]\}_2$	128–131 dec	34.02	6.44	16.74	33.85	6.26	16.54	847	830[b]
trans-$PtCl_2(py)[As(t\text{-}Bu)_3]$[c]	170–173 dec	34.52	5.47	11.81	34.34	5.54	11.65	591	581[b]
$[AsPh_4][PtCl_3As(t\text{-}Bu)_3]$[d]	176–180 dec	46.43	5.10	11.42	46.50	4.98	11.20		
cis-$PtCl_2(CO)[As(t\text{-}Bu)_3]$	>140 dec	28.90	5.05	13.12	28.76	4.88	12.92	540	525[e]
$[P(t\text{-}Bu)_3H][PtCl_3As(t\text{-}Bu)_3]$	173–176 dec	38.37	7.40	14.16	38.60	7.56	13.82		
$\{PdCl_2[P(t\text{-}Bu)_3]\}_2$	180–185 dec	37.96	7.18	18.67	38.10	7.26	18.10	759	740[e]
$PtCl[P(t\text{-}Bu)_2CMe_2CH_2]As(t\text{-}Bu)_3$	230–235 dec	42.50	7.89	5.23	42.71	7.92	5.00	678	656

[a] Uncorrected. [b] In dichloroethane. [c] % N: calcd, 2.37; found, 2.28. [d] Conductance of 10^{-3} M solution in dichloromethane: 42 Ω^{-1} cm^2 mol^{-1}. [e] In benzene.

tert-butylarsine complexes of platinum(II) and palladium(II) chlorides are reported herein. At the outset of this work, studies on complexes of bulky arsines with platinum metals were limited to the work of Shaw and co-workers,[10] who prepared the complexes *trans*-MCl_2L_2 where L = As(*t*-Bu)$_2$(*o*-tolyl) and As(*t*-Bu)(*o*-tolyl)$_2$ and M = Pt or Pd. The platinum(II) complexes were found to undergo intramolecular metalation on heating, but the palladium(II) complexes decomposed under similar conditions. While this work was in progress, a brief report[11] appeared on platinum(II) and palladium(II) complexes of trimesitylarsine.

Results and Discussion

Tri-*tert*-butylarsine readily reacts with platinum(II) chloride or potassium tetrachloroplatinate(II) to give the 2:1 complex *trans*-$PtCl_2[As(t\text{-}Bu)_3]_2$ (I) or the 1:1 dinuclear complex $Pt_2(\mu\text{-}Cl)_2Cl_2[As(t\text{-}Bu)_3]_2$ (II), depending upon the arsine to platinum mole ratio. The reaction of tri-*tert*-butylphosphine with platinum(II) chloride results in the formation of the internally metalated complex *trans*-$PtCl[P(t\text{-}Bu)_2CMe_2CH_2]P(t\text{-}Bu)_3$,[5a] and the reaction of the stibine affords only the 1:1 dinuclear complex $Pt_2(\mu\text{-}Cl)_2Cl_2[Sb(t\text{-}Bu)_3]_2$.[9] Thus, there appears to be significant differences in the reactions of tri-*tert*-butylphosphine, -arsine, and -stibine with platinum(II) chloride. Treatment of tri-*tert*-butylarsine with palladium(II) chloride or alkali metal tetrachloropalladate(II) gave only the 1:1 dinuclear complex $Pd_2Cl_2(\mu\text{-}Cl)_2[As(t\text{-}Bu)_3]_2$ (III), even with a large excess of the arsine and a prolonged reaction time. The behavior of tri-*tert*-butylarsine toward palladium(II) is, therefore, similar[9] to that of tri-*tert*-butylstibine but is markedly different than that of tri-*tert*-butylphosphine, which forms the isolable 2:1 complex *trans*-$PdCl_2[P(t\text{-}Bu)_3]_2$.[5a] Since the steric effects in the complexes of tri-*tert*-butylphosphine, -arsine, and -stibine are expected to decrease in the order P > As > Sb, the failure to isolate the 2:1 complexes of the arsine and the stibine with palladium(II) chloride is surprising and cannot be attributed to steric effects only.

Complex I is an orange solid, soluble in benzene as well as polar solvents such as dichloromethane. II and III are brown-red and are only sparingly soluble in benzene but very soluble in dichloromethane.

The analytical data, melting points, and molecular weights (in benzene or 1,2-dichloroethane) for I, II, and III, shown in Table I, are in excellent agreement with the proposed formulations. The ^1H NMR chemical shifts and the infrared absorption bands due to the metal–chlorine stretching frequencies for the three complexes, listed in Table II, are also consistent with their assigned structures. The infrared spectrum for each complex, in the 4000–400-cm^{-1} region, showed bands similar to those observed for the free arsine;[12] the infrared bands in the 400–50-cm^{-1} region are listed in the Experimental Section. A comparison of these frequencies with those reported[13] for analogous platinum(II) or palladium(II) complexes provides clear-cut assignments for the Pt–Cl or Pd–Cl stretching frequencies. The trans structure for I follows from the observation of only one Pt–Cl stretching frequency and its high value (330 cm^{-1}), which is characteristic of chlorine trans to chlorine. The observed Pt–Cl and Pd–Cl stretching frequencies for II and III are consistent with a symmetrical trans structure (Figure 1). Bridge-cleavage reactions of II and III discussed later also provide support for this structure.

Table II. Infrared and ^1H NMR Data of Tri-*tert*-butylarsine Complexes[a]

complex	IR, cm^{-1} ν(M–Cl)	NMR, ppm solvent	NMR, ppm As(*t*-Bu)
trans-$PtCl_2[As(t\text{-}Bu)_3]_2$	330 vs	C_6D_6	1.77 S
$\{PtCl_2[As(t\text{-}Bu)_3]\}_2$	338 vs, 322 m, 266 s	CH_2Cl_2	1.60 S
$\{PdCl_2[As(t\text{-}Bu)_3]\}_2$	344 vs, 299 m, 260 s	CH_2Cl_2	1.67 S
trans-$PtCl_2(py)[As(t\text{-}Bu)_3]$	330 vs	$CDCl_3$	1.67 S[b]
$[AsPh_4][PtCl_3As(t\text{-}Bu)_3]$	322 s, 275 s	$CDCl_3$	1.60 S[c]
cis-$PtCl_2(CO)[As(t\text{-}Bu)_3]$	344 s, 298 vs	C_6D_6	1.21 S
$[P(t\text{-}Bu)_3H][PtCl_3As(t\text{-}Bu)_3]$	322 vs, 276 vs	$CDCl_3$	1.66 S[d]
$PtCl[P(t\text{-}Bu)_2CMe_2CH_2]As(t\text{-}Bu)_3$	248 s	C_6D_6	1.55 S[e]

[a] Abbreviations: v, very; s, strong; m, medium; sh, shoulder; S, singlet; M, multiplet; D, doublet. [b] δ(py) 8.03 M. [c] δ(Ph) 7.23 M. [d] δ[P(*t*-Bu)] 1.73 D [^3J(P–H) = 14.7 Hz]. [e] δ[$P(t\text{-}Bu)_2CMe_2CH_2$]: *t*-Bu, 1.56 D [$J$(P–H) = 12.9 Hz]; CMe_2, 1.40 D [J(P–H) = 13.4 Hz]; CH_2, signals due to methylene protons could not be resolved due to the presence of other intense signals in the same region.

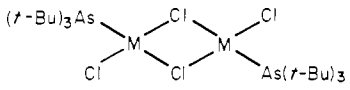

Figure 1.

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Unlike the platinum(II) or palladium(II) complexes of di-*tert*-butyl-*o*-tolylarsine,[10] *tert*-butyldi-*o*-tolylarsine,[10] and trimesitylarsine,[11] which undergo intramolecular metalation, neither I, II, nor III was found to undergo intramolecular metalation at room temperature or even upon heating. The ^{1}H NMR spectra of a benzene solution of I and dichloromethane solutions of II and III remained unchanged upon storing the solutions at room temperature, for 3 days. I was recovered unchanged when its solution in 2-propanol was refluxed for about 3 h; II and III decomposed under similar conditions.

Reactions of I. Ligand substitution as well as oxidative addition reactions of I with several substrates were examined. These investigations show that both As(t-Bu)$_3$ groups in I are readily displaced by py, $AsPh_3$, and tertiary phosphines such as PCy_3 and P(t-Bu)$_2$Ph. Only one As(t-Bu)$_3$ was displaced by CO or Cl^-, and no reaction occurred with C_2H_4. Unlike *trans*-$PtX_2(PR_3)_2$,[14] which readily undergoes oxidative addition with HCl, I did not react with HCl.

Treatment of I with excess (>2 mol) py, $AsPh_3$, PCy_3, and P(t-Bu)$_2$Ph afforded the previously known complexes *trans*-$PtCl_2(py)_2$, *cis*-$PtCl_2(AsPh_3)_2$, *trans*-$PtCl_2(PCy_3)_2$, and *trans*-$PtCl_2[P(t\text{-}Bu)_2Ph]_2$, respectively, in quantitative yields. All four complexes were characterized fully by elemental analyses and by infrared and ^{1}H and ^{31}P NMR spectral[15-17] measurements. Displacement of both the As(t-Bu)$_3$ ligands from I by $AsPh_3$ is unexpected and may be attributed to the insoluble nature of $PtCl_2(AsPh_3)_2$.

Complex I was readily converted into *cis*-$PtCl_2(CO)As(t\text{-}Bu)_3$ (IV) upon passing CO through its solution in THF at room temperature. One As(t-Bu)$_3$ was also displaced from I upon treatment with $AsPh_4Cl$ to give $[AsPh_4][PtCl_3As(t\text{-}Bu)_3]$ (V).

The analytical data for IV and V are given in Table I. The molecular nature of IV was confirmed by molecular weight measurement in benzene, and the proposed formulation of V as a 1:1 electrolyte was confirmed by conductance measurements in dichloromethane (Table I). The infrared spectrum of IV showed a strong band at 2080 cm^{-1} attributable to the terminal CO stretching frequency. This frequency shifted to 2025 cm^{-1} in the analogous complex containing ^{13}CO. The ^{13}C NMR spectrum of the ^{13}CO complex in dichloromethane showed resonance at 158.6 ppm with $^1J(^{195}Pt\text{–}^{13}C)$ = 1717 Hz due to ^{13}CO. The observed values for the CO stretching frequency, ^{13}C NMR chemical shift, and $^1J(^{195}Pt\text{–}^{13}C)$ are similar to those reported for the complexes *cis*-$PtCl_2(CO)AsR_3$,[19] where R_3 = Ph_3, $MePh_2$, or Et_3. Therefore, a cis structure is proposed for IV, which is also consistent with the observation of two Pt–Cl stretching frequencies in its infrared spectrum (Table II). The ^{1}H NMR spectrum of IV in benzene-d_6 showed a single resonance at 1.21 ppm. The infrared spectrum of V showed two strong bands at 325 and 275 cm^{-1} due to Pt–Cl stretching frequencies. As shown in Table II, the ^{1}H NMR spectrum of V in $CDCl_3$ showed a singlet and a multiplet due to the *tert*-butyl and phenyl protons, respectively, in the expected intensity ratio.

Reactions of II and III. Treatment of II with pyridine, in a 1:2 mole ratio, afforded *trans*-$PtCl_2(py)[As(t\text{-}Bu)_3]$ (VI). The analytical and molecular weight data for VI are given in Table I, and the ^{1}H NMR data and the Pt–Cl stretching frequency (infrared) are given in Table II. As shown by the data in Table II, the Pt–Cl stretching frequency for VI is similar to that for I and is consistent with the proposed trans structure.[13,18] The reaction of III with pyridine, under similar conditions, gave *trans*-$Pd(py)_2Cl_2$ and unreacted III. This is in contrast to the reaction of $Pd_2(\mu\text{-}Cl)_2Cl_2[P(t\text{-}Bu)_2Ph]_2$ with pyridine, which results in the formation of *trans*-$PdCl_2(py)[P(t\text{-}Bu)_2Ph]$.[18]

The chloride bridges in II are readily cleaved upon bubbling CO into its solution in dichloromethane to give IV in quantitative yield. However, III reacts with CO reversibly. The red solution of III in dichloromethane turned yellow-orange within a few minutes after bubbling with CO. The infrared spectrum of the solution showed a strong band at 2108 cm^{-1} due to the CO stretching frequency. The ^{13}C NMR spectrum of a dichloromethane solution of III after it was bubbled with ^{13}CO showed a resonance at 173.0 ppm due to the coordinated ^{13}CO and another resonance at 32.9 ppm due to As(t-Bu)$_3$. The infrared and the ^{13}C NMR data provide convincing evidence[19] for the formation of *trans*-$PdCl_2(CO)As(t\text{-}Bu)_3$ according to the reaction represented by eq 1. Evaporation of

$$\textit{trans}\text{-}Pd_2(\mu\text{-}Cl)_2Cl_2[As(t\text{-}Bu)_3]_2 + 2CO \rightarrow 2\,\textit{trans}\text{-}PdCl_2(CO)[As(t\text{-}Bu)_3] \quad (1)$$

the solution in vacuo gave a dark red solid that was found to be III as shown by the analytical, infrared, and ^{1}H NMR spectral data. These results clearly show that the reaction of III with CO is completely reversible.

Interaction of III with $AsPh_3$ in a 1:2 molar ratio surprisingly afforded *trans*-$PdCl_2(AsPh_3)_2$ instead of the expected mixed-ligand complex $PdCl_2(AsPh_3)[As(t\text{-}Bu)_3]$.

Treatment of II or III with excess (>4 mol) P(t-Bu)$_2$Ph or PCy_3 resulted in the formation of the complexes *trans*-$MCl_2(PR_3)_2$ [M = Pt or Pd, R_3 = (t-Bu)$_2$Ph or Cy_3] according to the reaction represented by eq 2.

$$M_2(\mu\text{-}Cl)_2Cl_2[As(t\text{-}Bu)_3]_2 + 4PR_3 \rightarrow 2\,\textit{trans}\text{-}MCl_2(PR_3)_2 + 2As(t\text{-}Bu)_3 \quad (2)$$

Reactions of II with P(t-Bu)$_2$Ph, PCy_3, or P(t-Bu)$_3$, in 1:2 mole ratio, were, however, not so straightforward and gave mixtures of products that proved difficult to separate. Thus, treatment of II with 2 equiv of P(t-Bu)$_2$Ph or PCy_3 gave a mixture of predominantly *trans*-$PtCl_2(PR_3)_2$ and $Pt_2(\mu\text{-}Cl)_2Cl_2(PR_3)_2$ [R_3 = (t-Bu)$_2$Ph or Cy_3], which could not be completely separated. For each reaction, the products were unequivocally characterized by comparing their ^{31}P NMR spectra with those for the authentic samples.[20] The ^{31}P{^{1}H} NMR spectrum of the product with PCy_3 showed resonances at 16.1 ppm [^1J(Pt–P) = 2400 Hz] and 20.6 ppm [^1J(Pt–P) = 3867 Hz] due to *trans*-$PtCl_2(PCy_3)_2$ and $Pt_2(\mu\text{-}Cl)_2Cl_2(PCy_3)_2$,[21] respectively. Similarly, the ^{31}P{^{1}H} NMR spectrum of the product of the reaction of II with P(t-Bu)$_2$Ph showed a resonance at 41.9 ppm [^1J(Pt–P) = 2543.8 Hz] due to *trans*-$PtCl_2[P(t\text{-}Bu)_2Ph]_2$ and another at 39.5 ppm [^1J(Pt–P) = 4068.4 Hz], which, by analogy with the ^{31}P NMR data for

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(20) The authentic samples of *trans*-$PtCl_2(PR_3)_2$ [R_3 = Cy_3 or (t-Bu)$_2$Ph] were prepared as in ref 16. The ^{31}P{^{1}H} NMR values for an authentic sample of $Pt_2(\mu\text{-}Cl)_2Cl_2(PCy_3)_2$ were obtained from ref 22.
(21) Although the complete ^{31}P spectrum (consisting of 19 lines) as found for $Pt_2Cl_4(PBu_3)_2$ [A. A. Kiffen, C. Masters, and J. P. Visser, *J. Chem. Soc., Dalton Trans.*, 1311 (1975)] was not observed due to low solubility of $Pt_2(\mu\text{-}Cl)_2Cl_2(PCy_3)_2$ in dichloromethane, the peak at 20.6 ppm was accompanied by a low-intensity peak at 20.2 ppm [^1J(Pt–P) = 3857 Hz] indicating the presence of both the symmetrical and antisymmetrical isomers.

$Pt_2(\mu\text{-}Cl)_2Cl_2(PCy_3)_2$, is assigned to $Pt(\mu\text{-}Cl)_2Cl_2[P(t\text{-}Bu)_2Ph]_2$. For the examination of the course of this reaction $^{31}P\{^1H\}$ NMR spectra of a solution containing II and $P(t\text{-}Bu)_2Ph$, in a 1:2 mole ratio in dichloromethane, were examined periodically. The spectrum soon after the reactants were mixed showed resonances at 41.9 ppm [^1J(Pt–P) = 2544 Hz] and 34.9 ppm [^1J(Pt–P) = 3002.9 Hz] in a ratio of ~2.5:1, respectively. The former resonance is due to *trans*-$PtCl_2[P(t\text{-}Bu)_2Ph]_2$. The latter resonance can be assigned to the complex *trans*-$PtCl_2[As(t\text{-}Bu)_3][P(t\text{-}Bu)_2Ph]$ by comparing the magnitude of ^1J(Pt–P), (which occurs in between the values for *trans*-$PtCl_2[P(t\text{-}Bu)_2Ph]_2$ and $Pt_2(\mu\text{-}Cl)_2Cl_2[P(t\text{-}Bu)_2Ph]_2$) with those for similar complexes.[22] After about 4 h, a new peak at ca. 39.5 ppm [^1J(Pt–P) = 4068.6 Hz] appeared with concomitant decrease in the intensity of the peak at 34.9 ppm. After ~3 days the intensities of the peaks at 34.9 and 39.5 ppm became almost equal, but the spectrum contained an additional resonance of weak intensity at 29.6 ppm, which we cannot assign at present. The spectrum did not change any further even after about 6 days. Although attempts to separate the components proved unsuccessful, the spectral data show that II reacts with $P(t\text{-}Bu)_2Ph$ according to reactions 3–5.

$$Pt_2(\mu\text{-}Cl)_2Cl_2[As(t\text{-}Bu)_3]_2 + 2P(t\text{-}Bu)_2Ph \rightarrow 2\,trans\text{-}PtCl_2[As(t\text{-}Bu)_3][P(t\text{-}Bu)_2Ph] \quad (3)$$

$$trans\text{-}PtCl_2[As(t\text{-}Bu)_3][P(t\text{-}Bu)_2Ph] + P(t\text{-}Bu)_2Ph \rightarrow trans\text{-}PtCl_2[P(t\text{-}Bu)_2Ph]_2 + As(t\text{-}Bu)_3 \quad (4)$$

$$2\,trans\text{-}PtCl_2[As(t\text{-}Bu)_3][P(t\text{-}Bu)_2Ph] \rightleftharpoons Pt_2(\mu\text{-}Cl)_2Cl_2[P(t\text{-}Bu)_2Ph]_2 + 2As(t\text{-}Bu)_3 \quad (5)$$

The reaction of II with $P(t\text{-}Bu)_3$, in a 1:2 mole ratio, gave a mixture of predominantly two products[23] that could not be separated completely. They were, however, unequivocally characterized to be $[P(t\text{-}Bu)_3H][PtCl_3As(t\text{-}Bu)_3]$ and *trans*-$PtCl[P(t\text{-}Bu)_2CMe_2CH_2][As(t\text{-}Bu)_3]$ by comparison of the infrared and $^{31}P\{^1H\}$ NMR spectra of the mixture with those of the authentic samples prepared by the reactions 6 and 7. The infrared spectrum of $[P(t\text{-}Bu)_3H][PtCl_3As(t\text{-}Bu)_3]$

$$Pt_2(\mu\text{-}Cl)_2Cl_2[As(t\text{-}Bu)_3]_2 + 2[P(t\text{-}Bu)_3H]Cl \rightarrow 2[P(t\text{-}Bu)_3H][PtCl_3As(t\text{-}Bu)_3] \quad (6)$$

$$\{PtCl[P(t\text{-}Bu)_2CMe_2CH_2]\}_2 + 2As(t\text{-}Bu)_3 \rightarrow 2\,trans\text{-}PtCl[P(t\text{-}Bu)_2CMe_2CH_2]As(t\text{-}Bu)_3 \quad (7)$$

showed a strong band at 2345 cm^{-1} and a medium band at 875 cm^{-1} due to the P–H stretching and bending frequencies,[5a] respectively. It also showed strong bands at 322 and 276 cm^{-1}, which, by comparison with the assignments[13] for $[PtCl_3AsEt_3]^-$, can be attributed to the stretching frequencies of Pt–Cl bonds trans to Cl and $As(t\text{-}Bu)_3$, respectively. Its $^{31}P\{^1H\}$ NMR spectrum consisted of a single peak at 42.8 ppm, which agrees well with the value reported[5a] for $[P(t\text{-}Bu)_3H][ZnCl_3P(t\text{-}Bu)_3]$. The $^{31}P\{^1H\}$ spectrum of $PtCl[P(t\text{-}Bu)_2CMe_2CH_2][As(t\text{-}Bu)_3]$ showed a resonance at −10.8 ppm [^1J(Pt–P) = 2768.6 Hz], which is characteristic[5a,6c] of platinum(II) complexes containing the $P(t\text{-}Bu)_2CMe_2CH_2$– group. Its infrared spectrum showed a strong band at 248 cm^{-1} due to the Pt–Cl stretching frequency; the low value of ν(Pt–Cl) is consistent[5a,24] with a structure having a Pt–Cl bond trans to a Pt–C bond. The formation of $[P(t\text{-}Bu)_3H][PtCl_3As(t\text{-}Bu)_3]$ and $PtCl[P(t\text{-}Bu)_2CMe_2CH_2][As(t\text{-}Bu)_3]$ in the reaction of II with $P(t\text{-}Bu)_3$ may be explained in terms of eq 8–11.

$$Pt_2(\mu\text{-}Cl)_2Cl_2[As(t\text{-}Bu)_3]_2 + 2P(t\text{-}Bu)_3 \rightarrow 2\,trans\text{-}PtCl_2[As(t\text{-}Bu)_3][P(t\text{-}Bu)_3] \quad (8)$$

$$trans\text{-}PtCl_2[As(t\text{-}Bu)_3][P(t\text{-}Bu)_3] \rightarrow HCl + trans\text{-}PtCl[P(t\text{-}Bu)_2CMe_2CH_2][As(t\text{-}Bu)_3] \quad (9)$$

$$P(t\text{-}Bu)_3 + HCl \rightarrow [P(t\text{-}Bu)_3H]Cl \quad (10)$$

$$2[P(t\text{-}Bu)_3H]Cl + Pt_2(\mu\text{-}Cl)_2Cl_2[As(t\text{-}Bu)_3]_2 \rightarrow 2[P(t\text{-}Bu)_3H][PtCl_3As(t\text{-}Bu)_3] \quad (11)$$

Treatment of III with $P(t\text{-}Bu)_2Ph$ or $P(t\text{-}Bu)_3$, in a 1:2 mole ratio, gave the red chloro-bridged dinuclear complexes $Pd_2(\mu\text{-}Cl)_2Cl_2(PR_3)_2$ [R_3 = $(t\text{-}Bu)_2Ph$ (VII) or $(t\text{-}Bu)_3$ (VIII)]. The infrared, ^1H NMR, and $^{31}P\{^1H\}$ NMR spectra of VII were identical with those reported by Shaw and co-workers.[18] The $^{31}P\{^1H\}$ spectrum of the previously unknown VIII showed a singlet at 122.7 ppm, and its infrared spectrum showed the expected[13,18] bands due to the Pd–Cl stretching frequencies at 340 s, 315 sh, and 250 s cm^{-1}. VIII undergoes intramolecular metalation in the solid state as well as in solution. Elemental analysis of a sample of VIII changed upon storing for about 1 week, and its $^{31}P\{^1H\}$ NMR spectrum showed the presence of VIII as well as the dimetalated complex $\{PdCl[P(t\text{-}Bu)_2CMe_2CH_2]\}_2$ (IX) in ~20:1 ratio, respectively. IX, however, was the sole product when a sample of VIII was kept in a mixture of dichloromethane/methanol for ~30 h as shown by its $^{31}P\{^1H\}$ NMR spectrum. IX has been recently[25] prepared from $PdCl[P(t\text{-}Bu)_2CMe_2CH_2][P(t\text{-}Bu)_3]$.

The reaction of III with PCy_3, in a 1:2 mole ratio, surprisingly, gave only *trans*-$PdCl_2(PCy_3)_2$ and unreacted III; there was no evidence for the formation of either $Pd_2(\mu\text{-}Cl)_2Cl_2(PCy_3)_2$ or *trans*-$PdCl_2[As(t\text{-}Bu)_3][PCy_3]$. Attempts to prepare the latter compounds according to reaction 12 also failed; reactants were recovered unchanged.

$$Pd_2(\mu\text{-}Cl)_2Cl_2[As(t\text{-}Bu)_3] + 2PdCl_2(PCy_3)_2 \xrightarrow[2\text{ days}]{CH_2Cl_2} Pd_2(\mu\text{-}Cl)_2Cl_2(PCy_3)_2 + 2\,trans\text{-}PdCl_2[As(t\text{-}Bu)_3](PCy_3) \quad (12)$$

Experimental Section

All operations involved in the preparation and subsequent reactions of tri-*tert*-butylarsine,[12] tri-*tert*-butylphosphine,[5a] di-*tert*-butylphenylphosphine,[18] and tricyclohexylphosphine (Strem Chemicals) were carried out under an atmosphere of oxygen-free dry argon or nitrogen with use of Vacuum Atmospheres Corp. drybox and standard vacuum line techniques. $PtCl_2$ and $PdCl_2$ were supplied by Johnson Mathey and Mallory Ltd. The solvents were dried by conventional methods and stored over molecular sieves. The carbon monoxide from Matheson was purified by passing through a column of KOH pellets.

Physical Measurements. Elemental analyses were performed by Guelph Chemical Laboratory, Guelph, Ontario. Melting points were determined with a Gallenkamp melting point apparatus and are uncorrected. Infrared spectra were determined with a Perkin-Elmer 180 double-beam spectrophotometer using KBr, KRS-5, or polyethylene demountable cells. Spectra in the solid state were obtained with samples prepared as mulls in Nujol. ^1H NMR spectra were recorded either on a Varian A60 or a Varian EML39 or a Bruker WP60 FT spectrometer; the reported chemical shifts are in ppm with

(22) G. K. Anderson, H. C. Clark, and J. A. Davies, *Inorg. Chem.*, **20**, 944 (1980).

(23) Traces of $PtCl[P(t\text{-}Bu)_2CMe_2CH_2][P(t\text{-}Bu)_3]$ (probably formed by the ligand displacement reaction of *trans*-$PtCl[P(t\text{-}Bu)_2CMe_2CH_2][As(t\text{-}Bu)_3]$ with $P(t\text{-}Bu)_3$) and $\{PtCl[P(t\text{-}Bu)_2CMe_2CH_2]\}_2$ (probably due to the metalation of $PtCl[P(t\text{-}Bu)_2CMe_2CH_2][P(t\text{-}Bu)_3]$[6c]) along with unreacted I (as shown by ^1H NMR) are also formed as shown by the ^{31}P NMR spectrum.

(24) A. J. Cheney, B. E. Mann, B. L. Shaw, and R. M. Slade, *J. Chem. Soc. A*, 3833 (1971); A. J. Cheney and B. L. Shaw, *ibid.*, 754, 860 (1972).

(25) H. C. Clark, A. B. Goel, and S. Goel, *Inorg. Chem.*, **18**, 2803 (1979).

reference to internal Me_4Si (positive values are downfield from Me_4Si). $^{31}P\{^1H\}$ spectra were measured with a Bruker WP60 FT spectrometer using 85% H_3PO_4 as external reference; positive δ values are downfield from 85% H_3PO_4. $^{13}C\{^1H\}$ spectra were recorded on a Bruker WP60 FT spectrometer using Me_4Si as internal reference; positive δ values are downfield from Me_4Si. Molecular weights were determined either in benzene or 1,2-dichloroethane with a Hitachi Perkin-Elmer 115 osmometer.

Reactions of As(*t*-Bu)$_3$ with $PtCl_2$ or K_2PtCl_4. (a) A solution of As(*t*-Bu)$_3$ (2.1 mmol) in THF (10 mL) was slowly added to a suspension of $PtCl_2$ (1 mmol) in the same solvent (20 mL) at room temperature, and the mixture was stirred for ~4 h. The resulting red solution was filtered, and the filtrate was concentrated in vacuo to give orange *trans*-$PtCl_2$[As(*t*-Bu)$_3$]$_2$: yield >90%; IR (400–50 cm^{-1}) 330 vs, 262 w, 176 w, 141 w, 122 w, 70 w, 65 w, 62 w.

(b) To a solution of K_2PtCl_4 (1 mmol) in a minimum amount of water was added a solution of As(*t*-Bu)$_3$ (2.2 mmol) in absolute ethanol (10 mL). The reaction mixture was stirred for ~4 h at room temperature and then filtered to give an orange solid, which was washed with water (2 × 3 mL) and ethanol (5 mL). Recrystallization of the solid from benzene/hexane gave orange crystals of *trans*-$PtCl_2$[As(*t*-Bu)$_3$] in ~70% yield.

(c) To a well-stirred suspension of $PtCl_2$ (2.1 mmol) in dichloromethane (25 mL) was added dropwise (~3 h) a solution of As(*t*-Bu)$_3$ (2 mmol) in the same solvent (15 mL). The reaction mixture was stirred for ~12 h and then filtered to remove any unreacted $PtCl_2$. The filtrate was concentrated under reduced pressure, and the resulting solid was washed with benzene (2 mL) and hexane (3 × 5 mL) and recrystallized from dichloromethane/methanol to give brown-red crystals of $Pt_2(\mu\text{-}Cl)_2Cl_2$[As(*t*-Bu)$_3$]$_2$ (II): yield ~90%; IR (400–50 cm^{-1}) 338 vs, 322 m, 266 s, 220 s, sh, 182 w, 137 w, 128 w, 94 w, 70 w.

Reactions of As(*t*-Bu)$_3$ with $PdCl_2$. (a) A solution of As(*t*-Bu)$_3$ (2 mmol) in dichloromethane or THF (10 mL) was slowly added to a suspension of $PdCl_2$ (2 mmol) in the same solvent (20 mL). The reaction mixture was stirred for ~5 h at room temperature. Removal of the solvent under reduced pressure and recrystallization of the resulting solid from dichloromethane/hexane gave brown-red $Pd_2(\mu\text{-}Cl)_2Cl_2$[As(*t*-Bu)$_3$]$_2$ (III): ~90% yield; IR (400–50 cm^{-1}) 344 vs, 299 m, 260 s, 208 s, sh, 176 w, 138 w, 123 sh, 89 m, 70 w.

(b) When the same reaction was carried out with use of a large excess of As(*t*-Bu)$_3$, only III was obtained in >90% yield.

Reactions of I, II, and III with CO. (a) CO (or ^{13}CO) was bubbled into a solution of I (0.2 g) in THF (5 mL) until the orange solution became yellow (~3 min). The volatiles were removed in vacuo, and the residue was washed with cold hexane (2 × 3 mL) to give pale yellow *cis*-$PtCl_2(CO)$[As(*t*-Bu)$_3$] in >90% yield. Removal of hexane from the filtrate gave As(*t*-Bu)$_3$, which was characterized by its ^1H NMR spectrum.

(b) *cis*-$PtCl_2CO$[As(*t*-Bu)$_3$] was obtained in quantitative yield when CO was passed through a solution of II (0.2 g) in dichloromethane and the resulting yellow solution was concentrated under reduced pressure.

(c) A red solution of III (0.2 g) in dichloromethane (10 mL) turned yellow-orange when CO was passed through it for ~5 min. The infrared spectrum of the solution showed the presence of coordinated CO. Removal of the solvent in vacuo and washing of the resulting solid with hexane (3 × 5 mL), however, gave III. In another experiment ^{13}CO was bubbled into a solution of III in dichloromethane until the color changed to yellow-orange. The infrared and ^{13}C NMR spectra of the solution were recorded, which indicated the presence of *trans*-$PdCl_2CO$[As(*t*-Bu)$_3$].

Reactions of I, II, and III with py. (a) I (0.2 mmol) and py (0.4 mmol) were stirred (~30 min) in THF (10 mL) at room temperature. Evaporation under reduced pressure and recrystallization of the resulting residue from dichloromethane/hexane gave orange *trans*-$PtCl_2$(py)[As(*t*-Bu)$_3$] in >75% yield.

(b) A mixture of I (0.2 mmol), py (2 mL), and THF (10 mL) was refluxed for ~24 h. Working up of the reaction mixture as above gave yellow *trans*-$PtCl_2(py)_2$: yield ~80%; IR ν(Pt–Cl) 342 cm^{-1}. Anal. Calcd for $C_{10}H_{10}N_2Cl_2Pt$: C, 28.31; H, 2.38. Found: C, 28.46; H, 2.47.

(c) To a solution of II (0.2 mmol) in dichloromethane (15 mL) was added dropwise a solution of py (0.4 mmol) in the same solvent. The reaction mixture was stirred for 1 h, and the solvent was evaporated in vacuo. Recrystallization of the residue from dichloromethane/hexane gave orange *trans*-$PtCl_2$(py)[As(*t*-Bu)$_3$], yield >78%.

(d) Pyridine (0.5 mmol) in THF (3 mL) was slowly added to III (0.2 mmol) in the same solvent (~15 mL), and the mixture was stirred for ~1 h. The solvent was removed under vacuum, and the residue was recrystallized from dichloromethane/methanol to give dark yellow needles of *trans*-$PdCl_2(py)_2$: yield 90%; IR ν(Pd–Cl) 352 cm^{-1}. Anal. Calcd for $C_{10}H_{10}N_2Cl_2Pd$: C, 35.80; H, 3.01; Cl, 21.13. Found: C, 35.72; H, 2.94; Cl, 21.54.

(e) To a solution of III (0.2 mmol) in dichloromethane (20 mL) was added dropwise a solution of pyridine (0.4 mmol) in the same solvent (10 mL). The reaction mixture was stirred for ~24 h. Removal of the solvent under reduced pressure gave a brown solid which, even after repeated recrystallizations from dichloromethane/hexane, was found to be a mixture of *trans*-$PdCl_2(py)_2$ and III as shown by the ^1H NMR and IR data.

Reactions of I and III with $AsPh_3$. (a) $AsPh_3$ (0.5 mmol) was stirred (~1 h) with I (0.2 mmol) in THF (10 mL). Removal of the solvent and recrystallization of the residual solid from dichloromethane/methanol gave *cis*-$PtCl_2(AsPh_3)_2$: yield >90%; IR ν(Pt–Cl) 349 m, 338 m cm^{-1} [lit.[17] ν(Pt–Cl) 349, 339 cm^{-1}]. Anal. Calcd for $C_{36}H_{30}Cl_2As_2Pt$: C, 49.22; H, 3.45. Found: C, 49.40; H, 3.52. As(*t*-Bu)$_3$ was recovered from the filtrate and characterized by its ^1H NMR spectrum.

(b) A solution of $AsPh_3$ (0.4 mmol) in dichloromethane (5 mL) was added dropwise to III (0.2 mmol). The solvent was removed under reduced pressure, and the residue was crystallized twice from dichloromethane/hexane to give orange *trans*-$PdCl_2(AsPh_3)_2$: ~70% yield; IR ν(Pd-Cl) 360 m [lit.[17] ν(Pd–Cl) 360 m]. Anal. Calcd for $C_{36}H_{30}Cl_2As_2Pd$: C, 54.74; H, 3.84. Found: C, 54.82; H, 3.76. Unreacted III (0.07 mmol) was recovered from the filtrates.

Reactions of I, II, and III with PCy_3. (a) I (0.2 mmol) and PCy_3 (0.45 mmol) were stirred together in THF (10 mL) at room temperature. After the reaction mixture was stirred for ~4 h, the solid was filtered and washed with pentane (2 × 5 mL). Recrystallization from dichloromethane gave pale yellow *trans*-$PtCl_2(PCy_3)_2$: yield >95%; mp 320–326 °C; IR ν(Pt–Cl) 335 cm^{-1} [lit.[16] mp >300 °C; ν(Pt–Cl) 335 cm^{-1}]; $^{31}P\{^1H\}$ NMR (CH_2Cl_2) δ 16.1 [^1J(Pt–P) = 2399.9 Hz]. Anal. Calcd for $C_{36}H_{66}P_2Cl_2Pt$: C, 52.28; H, 8.06. Found: C, 52.10; H, 7.92. Concentration of the filtrate gave As(*t*-Bu)$_3$, which was characterized by its ^1H NMR spectrum.

(b) PCy_3 (0.81 mmol) and II (0.2 mmol) were stirred (~1 h) together in dichloromethane (25 mL). Removal of the solvent under vacuum and subsequent washing of the residue with pentane (4 × 5 mL) gave pale yellow *trans*-$PtCl_2(PCy_3)_2$ in >90% yield, which was characterized as above.

(c) A solution of PCy_3 (0.41 mmol) in dichloromethane (5 mL) was slowly added (~1 h) to II (0.2 mmol) in the same solvent (20 mL). The solvent was removed in vacuo, and the residue was stirred in benzene (~10 mL) and filtered to remove *trans*-$PtCl_2(PCy_3)_2$. Removal of benzene and washing of the resultant solid with pentane (2 × 2 mL) followed by recrystallization from dichloromethane/methanol gave impure pale-orange $Pt_2(\mu\text{-}Cl)_2Cl_2(PCy_3)_2$ in ~40% yield.

(d) III (0.2 mmol) and PCy_3 (0.8 mmol) were stirred together in THF (15 mL). Removal of the solvent and recrystallization of the resulting product from dichloromethane/methanol gave yellow plates of *trans*-$PdCl_2(PCy_3)_2$: 90% yield; mp >250 °C dec; $^{31}P\{^1H\}$ NMR δ 24.6 (s). Anal. Calcd for $C_{36}H_{66}Cl_2P_2Pd$: C, 58.64; H, 9.06. Found: C, 58.34; H, 9.16.

(e) A solution of PCy_3 (0.4 mmol) in THF (10 mL) was added dropwise (2 h) to a suspension of III (0.2 mmol) in THF (15 mL). The reaction mixture was filtered to remove yellow *trans*-$PdCl_2(PCy_3)_2$ (0.06 mmol). The filtrate was concentrated in vacuo to give a brown-red residue that was found to be a mixture of *trans*-$PdCl_2(PCy_3)_2$ and III as shown by ^{31}P and ^1H spectral measurements.

Reaction of I, II, and III with P(*t*-Bu)$_2$Ph. (a) A mixture of I and P(*t*-Bu)$_2$Ph in a 1:2 mole ratio in THF was stirred for ~4 h. The solvent was removed, and the residue was recrystallized from dichloromethane/methanol to give yellow *trans*-$PtCl_2$[P(*t*-Bu)$_2$Ph]$_2$ in >90% yield: mp 235–238 °C; IR ν(Pt–Cl) 337 cm^{-1} [lit.[18] mp 234–237 °C; ν(Pt–Cl) 337 cm^{-1}]; $^{31}P\{^1H\}$ NMR (CH_2Cl_2) δ 41.9 [^1J(Pt–P) = 2543.9 Hz].

(b) A solution of P(*t*-Bu)$_2$Ph (1 mmol) in dichloromethane (5 mL) was added to II (0.2 mmol) in the same solvent (~15 mL). The reaction mixture was stirred for ~3 h. Removal of the solvent in vacuo afforded *trans*-$PtCl_2$[P(*t*-Bu)$_2$Ph]$_2$ in ~95% yield.

(c) To a solution of II (0.2 mmol) in dichloromethane (15 mL) was added dropwise at room temperature $P(t\text{-}Bu)_2Ph$ (0.4 mmol) in the same solvent (5 mL). The reaction mixture was stirred for ~1 h. The solvent was removed under reduced pressure to give a pale orange solid that was shown by ^{31}P NMR spectral measurement to be a mixture of *trans*-$PtCl_2[P(t\text{-}Bu)_2Ph]_2$ and $Pt_2(\mu\text{-}Cl)_2Cl_2[P(t\text{-}Bu)_2Ph]_2$. The quantity of *trans*-$PtCl_2[P(t\text{-}Bu)_2Ph]_2$ increased with increasing rate of addition of the phosphine.

(d) III and $P(t\text{-}Bu)_2Ph$, in a 1:4 mole ratio, were stirred (~3 h) together in dichloromethane. Removal of the solvent in vacuo and crystallization of the residue from dichloromethane/methanol gave yellow crystals of *trans*-$PdCl_2[P(t\text{-}Bu)_2Ph]_2$: >90% yield: mp 221–225 °C dec; IR ν(Pd–Cl) 350 cm^{-1} [lit.[10] mp 222–226 °C dec; ν(Pd–Cl) 350 cm^{-1}]; $^{31}P\{^1H\}$ NMR (CH_2Cl_2) δ 52.9. Anal. Calcd for $C_{28}H_{46}P_2Cl_2Pd$: C, 54.1; H, 7.5. Found: C, 53.88; H, 7.6.

(e) $P(t\text{-}Bu)_2Ph$ (0.4 mmol) in THF (5 mL) was slowly added to a solution of III (0.2 mmol) in THF (10 mL). Removal of the solvent and repeated recrystallization of the resulting solid from dichloromethane/methanol gave dark red needles of $Pd_2(\mu\text{-}Cl)_2Cl_2[P(t\text{-}Bu)_2Ph]_2$ in ~70% yield: mp 220–224 °C dec; IR ν(Pd–Cl) 355 vs, 307 m, 250 vs cm^{-1} [lit.[10] mp 220–225 °C dec, ν(Pd–Cl) 356 vs, 307 m, 250 vs cm^{-1}]; $^{31}P\{^1H\}$ NMR (CH_2Cl_2) δ 74.4 (s). Anal. Calcd for $C_{28}H_{46}P_2Cl_4Pd_2$: C, 42.1; H, 5.8; Cl, 17.7. Found: C, 42.3, H, 5.9, Cl, 17.5.

Reactions of II and III with $P(t\text{-}Bu)_3$. (a) A solution of $P(t\text{-}Bu)_3$ (0.40 mmol) in THF (5 mL) was added dropwise to a suspension of II (0.20 mmol) in THF (15 mL) at room temperature. A clear orange-red solution was obtained. Removal of the volatiles in vacuo and washing of the residue with pentane (~30 mL) gave the pale brown solid $[Pt(t\text{-}Bu)_3H][PtCl_3As(t\text{-}Bu)_3]$, which, even after recrystallization from dichloromethane/pentane, was found to contain traces of II. The combined filtrate and washings, on concentration, yielded a yellowish solid. Recrystallization from acetone afforded slightly impure $PtCl[P(t\text{-}Bu)_2CMe_2CH_2]As(t\text{-}Bu)_3$ as shown by the infrared and $^{31}P\{^1H\}$ NMR spectral measurements.

(b) Addition of $P(t\text{-}Bu)_3$ (0.4 mmol) to a suspension of III (0.2 mmol) in THF (10 mL) gave a red solution. Removal of the volatiles under reduced pressure and washing of the residue with pentane (5 mL) gave red $Pd_2(\mu\text{-}Cl)_2Cl_2[P(t\text{-}Bu)_3]_2$: yield 85%; IR (Pd–Cl) 340 s, 315 sh, 250 s cm^{-1}.

Preparation of $\{PtCl[P(t\text{-}Bu)_2CMe_2CH_2]As(t\text{-}Bu)_3\}$. $\{PtCl[P(t\text{-}Bu)_2CMe_2CH_2]\}_2$[6c] (0.5 mmol) was stirred (~3 h) with $As(t\text{-}Bu)_3$ (1.10 mmol) in benzene (10 mL). The solvent was removed, and the resulting product was recrystallized from hexane to give colorless plates of *trans*-$PtCl[P(t\text{-}Bu)_2CMe_2CH_2][As(t\text{-}Bu)_3]$ in ~90% yield (see Tables I and II).

Preparation of $[P(t\text{-}Bu)_3H][PtCl_3As(t\text{-}Bu)_3]$. Equimolar amounts of II and $[P(t\text{-}Bu)_3H]Cl$ were stirred (~10 h) in THF at ~30 °C. Removal of the solvent and recrystallization of the residue from dichloromethane/hexane gave orange $[P(t\text{-}Bu)_3H]\{PtCl_3[As(t\text{-}Bu)_3]\}$, yield >80% (see Tables I and II).

Reaction of I with $AsPh_4Cl$. An equimolar mixture of I and $AsPh_4Cl$ was stirred together in THF for ~10 h at room temperature. Removal of the solvent under reduced pressure and crystallization of the residue with dichloromethane/hexane gave orange plates of $[AsPh_4][PtCl_3As(t\text{-}Bu)_3]$ in ~85% yield (see Tables I and II).

Attempted Reaction of I with $CH_2{=}CH_2$. Ethylene was bubbled into a solution of I in benzene for ~1 h at room temperature. There was no change in the ^1H NMR spectrum, and the removal of the volatiles afforded I quantitatively.

Attempted Reaction of I with HCl. A solution of I (0.2 mmol) in THF was stirred with HCl (0.6 mmol, produced by reacting acetyl chloride with methanol) at 0 °C for ~$^1/_2$ h. Removal of the volatiles gave unreacted I quantitatively.

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Registry No. I, 78610-08-9; II, 78610-09-0; III, 78610-10-3; IV, 78610-11-4; V, 78610-13-6; VI, 78610-14-7; VII, 34408-85-0; VIII, 77932-99-1; $PtCl[P(t\text{-}Bu)_2CMe_2CH_2]As(t\text{-}Bu)_3$, 78610-15-8; $[P(t\text{-}Bu)_3H][PtCl_3As(t\text{-}Bu)_3]$, 78610-17-0; *trans*-$PtCl_2(PCy_3)_2$, 60158-99-8; $Pt_2(\mu\text{-}Cl)_2Cl_2(PCy_3)_2$, 76156-54-2; *trans*-$PdCl_2(PCy_3)_2$, 78655-99-9; *trans*-$PtCl_2[P(t\text{-}Bu)_2Ph]_2$, 36319-68-3; $Pt_2(\mu\text{-}Cl)_2Cl_2[P(t\text{-}Bu)_2Ph]_2$, 78610-18-1; *trans*-$PdCl_2[P(t\text{-}Bu)_2Ph]_2$, 34409-44-4; $\{PtCl[P(t\text{-}Bu)_2CMe_2CH_2]\}_2$, 69393-57-3.

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Catalytic and Structural Studies of the Rhodium(I) Complexes of the norphos and renorphos Ligands

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Previously reported (−)-(*R*,*R*)-2-*exo*-3-*endo*-bis(diphenylphosphino)bicyclo[2.2.1]heptene (norphos) and its reduced congener (−)-(*R*,*R*)-2-*exo*-3-*endo*-bis(diphenylphosphino)bicyclo[2.2.1]heptane (renorphos) have been studied as chiral ligands for the Rh(I)-catalyzed reductions of prochiral substrates. It was found that reduction of the norphos to renorphos ligand occurs upon catalyst activation so that the ligand on the operating catalyst is renorphos, regardless of the precursor. High hydrogenation ee's (95%) were obtained with two enamide substrates but only moderate (63%) for itaconic acid. Crystal structure data at −100 °C: a = 15.765 (8) Å, b = 20.482 (9) Å, c = 11.317 (4) Å, orthorhombic, $P2_12_12_1$ (No. 16), Z = 4, R = 0.047, R_w = 0.048, absolute configuration determined, 3944 reflections with $I > 2.5\sigma_I$. X-ray data were collected at −100 °C on a Syntex $P2_1$ autodiffractometer with monochromated Mo Kα radiation. The norphos ligand chelates the Rh(I) center although it must suffer severe distortions in order to do so. The largest distortion is the change in dihedral angle PCCP from 120 to 64°. The bicyclo[2.2.1]heptene skeleton absorbs this drastic change in dihedral angle in smaller changes in dihedral and bond angles, as well as bond lengths.

There is extant a large amount of published work dealing with the design and synthesis of chiral diphosphines as ligands for transition metals [mainly Rh(I)] for asymmetric induction during catalytic transformations of organic molecules.[1] By far the most studied catalytic reaction is hydrogenation of enamides to give amino acid derivatives, and recent work by the Halpern,[2] Brown,[3] and Ojima[4a–c] groups has led to a good

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