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Chemistry of Low-Valent Zirconium Complexes with Tertiary Phosphines. Reversible CO Binding by Bis(η-butadiene)[1,2-bis(dimethylphosphino)ethane]zirconium

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Treatment of $ZrCl_4$ with 1,2-bis(dimethylphosphino)ethane (dmpe) affords $ZrCl_4(dmpe)_2$. Reduction of $ZrCl_4(dmpe)_2$ with Na/Hg in the presence of butadiene yields the dmpe-bridged dimer $[Zr(\eta\text{-}C_4H_6)_2(dmpe)]_2$(dmpe), which is in equilibrium with coordinatively unsaturated $Zr(\eta\text{-}C_4H_6)_2$(dmpe) and free dmpe. Treatment of $[Zr(\eta\text{-}C_4H_6)_2(dmpe)]_2$(dmpe) with CO at low temperatures gives thermally unstable $Zr(\eta\text{-}C_4H_6)_2$(dmpe)(CO), which decomposes under vacuum to $Zr(\eta\text{-}C_4H_6)_2$(dmpe). This complex forms adducts with a variety of small Lewis bases. Equilibrium constants for adduct formation have been measured by NMR techniques; trends in ΔH for adduct formation suggest that $Zr(\eta\text{-}C_4H_6)_2$(dmpe) prefers small, σ-donating ligands. $[Zr(\eta\text{-}C_4H_6)_2(dmpe)]_2$(dmpe) is a hydrogenation catalyst.

Tertiary phosphine complexes have generally proved more reactive than analogous compounds containing carbonyl, carbocyclic, or other electron-withdrawing ligands, particularly for reactions involving metalation of C–H bonds. For example, ML_4 [M = Fe,[1] Ru,[1b,d,2] or Os,[1b,d,2] L = PMe_3, L_2 = 1,2-bis(dimethylphosphino)ethane], IrL_4^+,[3] and PtL_4[4] derivatives insert into aromatic and certain sp^3 C–H bonds; carbonyl and cyclopentadienyl analogues are substantially less reactive. Similarly, NiL_4, PdL_4, and PtL_4 derivatives show enhanced reactivity to aryl halides.[5] These and related observations have prompted the preparation of a number of low-valent binary metal complexes of tertiary phosphine ligands, a program initiated by Chatt and co-workers.[1a,2] Despite indications that zerovalent group 4 metals might offer exceptionally reactive systems,[6] no report of binary phosphine complexes of Ti, Zr, or Hf has appeared. Complexes of Ti(0),[7] Ti(II),[6a,8,9] and Zr(II)[6b,10] with carbocyclic ligands have been prepared. Indeed, reports of unsuccessful attempts to prepare $Ti(dmpe)_3$ (dmpe = 1,2-bis(dimethylphosphino)ethane) have been published.[1a] We recently reported that Zr^{II}(dmpe) and Zr^0(dmpe) adducts could be prepared if a π-accepting ligand were present.[11]

This paper deals with the preparation of $Zr(C_4H_6)_2$(dmpe) complexes, their properties, and their reactivity.

Experimental Section

Manipulations were performed under vacuum or under an atmosphere of prepurified nitrogen or argon. Trimethylphosphine[12] and 1,2-bis(dimethylphosphino)ethane[13] were prepared by literature methods. Solvents were purified by distillation from sodium benzophenone ketyl. Butadiene and CO were dried by passage through a short tube packed with P_2O_5 or through a −78 °C trap, respectively. ^{1}H NMR (100 MHz), ^{31}P NMR (32.2 MHz), ^{13}C NMR (20.1 MHz), infrared, and mass spectra were obtained on Varian XL-100, Brüker WP-80, Varian CFT-20, Perkin-Elmer 457 A, and AEI MS-9 spectrometers, respectively. GLC analyses were performed on a Varian 920 gas chromatograph. ^{31}P and ^{13}C NMR chemical shifts are relative to external 85% phosphoric acid and tetramethylsilane, respectively. Elemental analyses were performed by Alfred Bernhardt Microanalytische Laboratorium, West Germany. Cryoscopic molecular weights were determined with an apparatus similar to that described by Bercaw.[6a]

Preparation of $ZrCl_4(dmpe)_2$ (1). Over a 30-min period 25 g (0.17 mol) of dmpe was added to a stirred suspension of 19.1 g (0.082 mol) of $ZrCl_4$ in 300 mL of benzene. During the addition, heat was evolved and nearly all the $ZrCl_4$ dissolved. After the solution was heated to near reflux for 15 min, it was filtered through a layer of Celite, and the filtrate was concentrated under vacuum to a volume of ~30 mL. Addition of 35 mL of hexane and cooling to −20 °C gave 30 g (0.057 mol, 70%) of white, crystalline **1**: mass spectrum *m/e* 530 $[^{12}C_{12}{}^1H_{32}{}^{31}P_4{}^{35}Cl_4{}^{90}Zr]^+$, 345 [$M^+$ − Cl − dmpe]; $^{31}P\{^1H\}$ NMR −2.7 (s) ppm.

Anal. Calcd for $C_{12}H_{32}P_4Cl_4Zr$: C, 27.03; H, 6.05; Cl, 26.60. Found: C, 27.33; H, 6.07; Cl, 26.66.

Preparation of $[(\eta\text{-}C_4H_6)_2Zr(dmpe)]_2$(dmpe) (2). To 10.0 g (18.8 mmol) of **1** dissolved in 250 mL of THF was added 1 kg of 0.75% Na/Hg. The mixture was cooled to −78 °C and 150 mmol of butadiene was distilled into the solution. After being warmed to room temperature, the mixture was shaken for 110 min, resulting in formation of a deep purple solution. The solution was decanted and the amalgam washed with an additional 125 mL of THF. The pooled extracts were filtered through a pad of Celite and evaporated to dryness. The residual brown solid was extracted with 150 mL of boiling hexane. After the purple solution was filtered and the filtrate cooled to −20 °C, the solvent was decanted, leaving dark crystals of **2**, which were washed with hexane and dried under vacuum: 6.9 g (8.1 mmol, 86%); mass spectrum *m/e* 348.0699 $[Zr(C_4H_6)_2(dmpe)]^+$ (calculated for $[^{12}C_{14}{}^1H_{28}{}^{31}P_2{}^{90}Zr]^+$, 348.0709); mol wt (cryoscopic in benzene) 280 ± 57; ^{1}H NMR (benzene-d_6) τ 9.89 (m, 4 H, HC=CH*H*), 9.12 (apparent triplet, 18 H, PCH_3), 8.69 (apparent doublet, 6 H, PCH_2), 8.35 (m, 4 H, CH=C*H*H), 4.32 (m, 4 H, C*H*=CH_2).

Anal. Calcd for $C_{17}H_{36}P_3Zr$: C, 48.09; H, 8.55; P, 21.88; Zr, 21.48. Found: C, 47.88; H, 8.27; P, 20.55; Zr, 21.91.

Reaction of 2 with HCl. A 50-mL flask containing 537.9 mg (0.634 mmol) of **2** was attached to a vacuum manifold. The vessel was cooled to −196 °C and evacuated. Toluene (5 mL) and 6.65 mmol of HCl were condensed onto the solid. After the mixture was allowed to warm to 25 °C and stirred for 3 h, the volatile components were distilled through traps at −78, −126, and −196 °C. Butene (2.23 mmol) was recovered from the −126 °C trap (identified by mass spectral and NMR analyses; the ratio of 1-butene to 2-butene was 2.2:1), corresponding to a recovery of 1.8 equiv/equiv of Zr. No hydrogen was evolved.

Reaction of 2 with O_2. Oxygen (4.0 equiv) was admitted to a vessel containing a stirred solution of 2.0 g (2.4 mmol) of **2** dissolved in 10 mL of toluene. After 10 h the purple color of **2** had faded and a slurry of a yellow solid remained. The volatile components were distilled through −78 and −196 °C traps. A 4.58-mmol quantity of butadiene (identified by comparison of its ^{1}H NMR spectrum with that of an authentic sample) was recovered from the −196 °C trap.

Pyrolysis of 2. A small flask containing 200.1 mg (0.24 mmol) of **2** was immersed in an oil bath and heated while any volatile components evolved were continuously pumped through −78 and −196 °C traps. Between 100 and 150 °C evolution of volatile products began and was accompanied by sublimation of a purple solid to the cooler parts of the vessel (later shown to be **3** by ^{1}H NMR measurements). At temperatures greater than 200 °C, condensable and noncondensable gases were evolved rapidly; the solid darkened and a metallic film was deposited on the walls of the flask. Dmpe, identified by its melting point and ^{1}H NMR spectrum, was recovered from the −78 °C trap; butene, identified by its mass spectrum, was recovered from the −196 °C trap. No butadiene was detected.

Hydrogenations with 2. An apparatus similar to that described by Schrock and Osborn[14] was used to monitor H_2 consumption at a constant pressure of 1 atm. The unsaturated compound (10–15 mmol) and a known volume of benzene (7–8 mL) were stirred under vacuum with a small amount of **2** in a flask attached and open to the hydrogenation apparatus. This was necessary in order to scavenge small amounts of water and oxygen present in the apparatus which would, otherwise, destroy the small concentrations of catalyst used for the hydrogenations. After 12–18 h the solvent and substrate were

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condensed into the hydrogenation flask, the temperature was adjusted to 25 ± 0.2 °C with a water bath, and the apparatus was filled with 1 atm of hydrogen. An aliquot of a stock solution of **2**, prepared by dissolving an accurately weighed portion of **2** in benzene (typically 200 mg/2.0 mL), was introduced via a syringe into the stirred solution through a septum-capped side arm on the hydrogen flask. Monitoring of hydrogen consumption with a gas buret was initiated immediately. Small samples were withdrawn occasionally for GLC analysis. In several cases an internal standard (*n*-heptane) was added to the olefin–benzene mixture prior to hydrogenation, in order to facilitate analysis. Aliquots were analyzed on a 25 ft × $^3/_8$ in. column of $AgNO_3$ (20%)/benzyl cyanide on Chromasorb P.

In one experiment, no olefin was added. A 430.6-mg (0.51 mmol) quantity of **2** in 5 mL of toluene consumed 1.96 mmol of H_2, corresponding to a consumption of 1.93 equiv of H_2/equiv of Zr. The resulting dark brown solution appeared homogeneous. The volatile components were distilled through −78 and −196 °C traps. Butane, as identified by mass spectroscopy, was recovered from the −196 °C trap.

Reactions of 2 with CO. I. Stoichiometry. A solution of 540 mg (0.637 mmol) of **2** in 20 mL of toluene was placed in a 50-mL flask and cooled to −78 °C, resulting in formation of a brown suspension. A measured excess (3.70 mmol) of CO was admitted to the reaction vessel, and the mixture was stirred rapidly while it warmed to −45 °C. After 2 h of stirring at −45 °C, the flask contained a yellow precipitate suspended in an orange solution. The mixture was cooled to −78 °C and the excess CO (identified by mass spectroscopy) was collected with a Toepler pump; 2.49 mmol was recovered, corresponding to a consumption of 0.95 equiv of CO/equiv of Zr. While collection of evolved gases was maintained with a Toepler pump, the stirred solution was warmed to −22 °C. After 2 h, 90% of the initially consumed CO had been recovered (identified as CO by mass spectroscopy). During this period, distillation of the solvent was prevented by fitting the reaction vessel with a dry ice condenser. Subsequent warming to 0 °C allowed recovery of a total of 1.17 mmol of CO, corresponding to a recovery of 97% of the amount consumed.

II. Isolation of (η-C_4H_6)$_2$Zr(dmpe)(CO) (5). A freshly filtered solution of 2.453 g (2.89 mmol) of **2** in 25 mL of toluene was cooled to −45 °C and placed under 1 atm of CO in a closed system. Consumption of CO was monitored by the pressure drop; occasionally, additional CO was added to maintain the pressure near 1 atm. After 2 h CO consumption had ceased, and the mixture was cooled to −78 °C. The yellow precipitate was collected by filtration at −78 °C. While the filter cake was maintained at this temperature, the solid was washed with three 10-mL portions of pentane and dried under vacuum, affording 1.82 g (4.83 mmol, 84%) of **5** as a pyrophoric, thermally unstable, yellow powder.

A sample of **5** (2.297 g) was allowed to decompose in the air and the residue was digested with hot, concentrated nitric acid, yielding a clear solution. After the solution was boiled to dryness several times with added distilled water, the residue was dissolved in 2 N H_2SO_4 and analyzed gravimetrically for Zr by precipitation of the phosphate complex and ignition to zirconium pyrophosphate.[15] A 1.564-g quantity of ZrP_2O_7 was obtained.

Anal. Calcd for $C_{15}H_{28}P_2OZr$: Zr, 24.16. Found: Zr, 23.43.

A ^{13}C-labeled derivative was prepared in situ for NMR studies by placing 80 mg of **2** and 2 mL of 3:1 toluene-d_8/THF with a magnetic stirring bar in a 10-mm tube. The solution was stirred at −45 °C for 2 h under an excess of 90% ^{13}CO. After this period the stirring bar was removed with the aid of a magnet and the tube was sealed. The sample was maintained at −78 °C prior to and during NMR measurements.

Preparation of Zr(η-C_4H_6)$_2$(dmpe) (3). A 50-mL flask, fitted with a dry ice condenser and attached to a vacuum manifold, was charged with 3.26 g (8.63 mmol) of **5**. Toluene (30 mL) was condensed into the vessel at −78 °C and the suspension warmed to −22 °C while the liberated CO was continuously collected with a Toepler pump. After the initial rapid evolution of CO had subsided, the mixture was warmed to 0 °C over a period of 3 h, affording a deep purple solution and a total of 7.34 mmol of evolved CO. The dry ice condenser was warmed to 25 °C, allowing the solvent to evaporate and leaving a purple solid. Crystallization of the residue from boiling hexane afforded 1.57 g (4.49 mmol, 52%) of **3** as purple crystals: mass spectrum *m/e* 348 [$^{12}C_{14}{}^1H_{28}{}^{31}P_2{}^{90}Zr$]$^+$, 294 [$M^+ - C_4H_6$]; ^{1}H NMR (benzene-$d_6$) τ 9.89 (m, 4 H, HC═C*H*H), 9.03 (apparent triplet, J_{HCP} = 3.0 Hz, 12 H, PCH_3), 8.63 (d, J_{HCP} = 14.0 Hz, 4 H, PCH_2), 8.32 (m, 4 H, HC═C*H*H), 4.63 (m, 4 H, *H*C═CH).

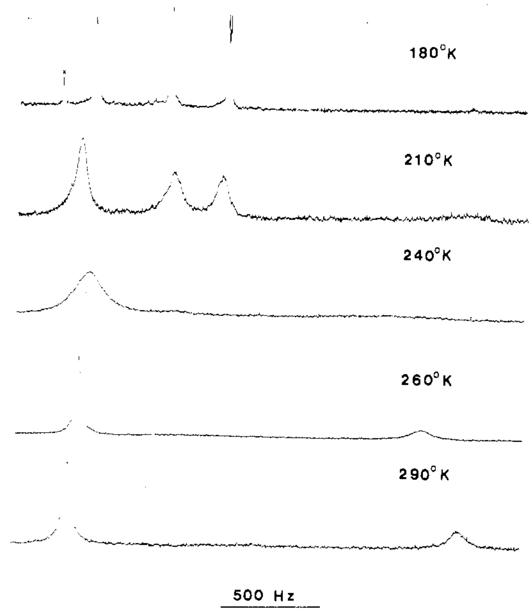


Figure 1. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of [(η-C_4H_6)$_2$Zr(dmpe)]$_2$(dmpe) in toluene-d_8/THF. The resonance marked with an × in the 180 K spectrum is a small amount of the monomer (η-C_4H_6)$_2$Zr(dmpe).

Anal. Calcd for $C_{14}H_{28}P_2Zr$: C, 48.11; H, 8.07; P, 17.72; Zr, 26.12. Found: C, 47.82; H, 7.86; P, 17.43; Zr, 26.58.

Lewis Base Adducts of 3 for NMR Measurements. In a typical experiment, 92 mg (0.264 mmol) of **3** was charged to a 10-mm tube, calibrated to allow direct reading of the liquid volume contained. The tube was evacuated and cooled to −196 °C. PMe_3 (0.326 mmol) and 2 mL of 3:1 toluene-d_8/THF were condensed onto the solid; the tube was sealed and allowed to warm. For each temperature of interest, the clear solution of **3** and the Lewis base contained within the tube was introduced into the precooled probe and allowed to thermally equilibrate. After measurement of the liquid volume, a spectrum was recorded. In this manner, it was possible to calculate the molarity of the components contained at different temperatures.

Other NMR samples were prepared similarly.

Results and Discussion

Preparation and Properties of [Zr(η-C_4H_6)$_2$(dmpe)]$_2$(dmpe). As indicated in eq 1, stirring $ZrCl_4$ and dmpe in aromatic

$$ZrCl_4 + 2dmpe \rightarrow \underset{\mathbf{1}}{ZrCl_4(dmpe)_2} \quad (1)$$

solvents affords $ZrCl_4(dmpe)_2$ (**1**). Presumably, **1** is structurally similar to the dodecahedral complexes of group 4 halides with *o*-phenylenebis(dimethylarsine) (diars),[16] one of which, $TiCl_4(diars)_2$, has been structurally characterized by X-ray methods.[16a] Complex **1** is a convenient starting material as it is highly soluble and resists brief exposure to the atmosphere. Reduction of **1** with Na/Hg in the presence of excess butadiene results in the formation of purple solutions from which brown crystals of [Zr(η-C_4H_6)$_2$(dmpe)]$_2$(dmpe) (**2**) can be isolated in good yield. The stoichiometry is established by analytical and ^{1}H NMR data, the latter showing only dmpe resonances and those characteristic of η^4-butadiene. The highest mass feature in the mass spectrum of **2** is one corresponding to Zr(C_4H_6)$_2$(dmpe), suggesting that **2** is the dmpe-bridged dimer indicated in eq 2. The ^{31}P NMR spectra

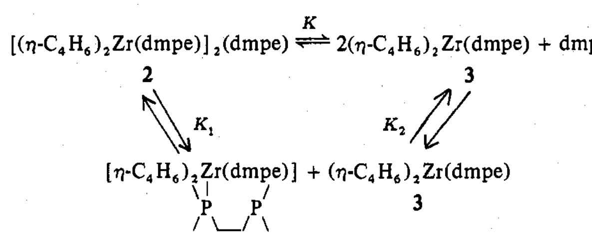
$$ZrCl_4(dmpe)_2 + \text{excess } C_4H_6 \xrightarrow[\text{Na/Hg}]{} \underset{\mathbf{2}}{[Zr(\eta\text{-}C_4H_6)_2(dmpe)]_2(dmpe)} \quad (2)$$

in Figure 1 indicate three chemically inequivalent phosphorus sites at low temperatures (^{31}P coupling is unresolved), consistent with the dmpe-bridged formulation, providing the ends of the chelating dmpe in each dimer half are chemically inequivalent. When spectra are recorded at warmer temperatures, the resonance at lowest field broadens and shifts to higher field; at temperatures near 25 °C this resonance sharpens and approaches the frequency of uncomplexed dmpe. The two resonances at intermediate field at low temperatures coalesce and shift to lower field when the sample is warmed. At room temperature, the two signals observed, one in the region of complexed dmpe and one at high field near free dmpe, have relative intensities of 2:1, respectively. These observations suggest that **2** is in equilibrium with a monomeric, 16-electron fragment, $Zr(\eta\text{-}C_4H_6)_2(dmpe)$ (**3**), and free dmpe, as shown in eq 3. At low temperatures, the equilibrium is

$$\underset{\text{brown}}{[(\eta\text{-}C_4H_6)_2Zr(dmpe)]_2(dmpe)} \rightleftharpoons \underset{\text{purple}}{2\underset{\mathbf{3}}{(\eta\text{-}C_4H_6)_2Zr(dmpe)}} + dmpe \quad (3)$$

shifted to the dimer and the ligand dissociation rate is slow; only resonances attributable to **2** are observed. As the temperature is raised, the anticipated positive ΔS for eq 3 shifts the equilibrium to the right and the exchange rate increases. At room temperature, the high-field resonance represents dmpe exchanging between uncomplexed sites and bridging sites in **2**, the relative populations of the sites depending on the magnitude of the equilibrium constant. The observation that this signal occurs near free dmpe at 25 °C implies that the equilibrium lies far to the right at this temperature. The low-field resonance at 25 °C represents the weighted average of chelating dmpe sites in **2** and **3**. Chelated dmpe and bridging dmpe do not exchange at a significant rate, as shown by the presence of distinct resonances at room temperature.

A more complete model allows stepwise dissociation of dmpe, as in eq 4. The inclusion of small or moderate con-



(4)

centrations of the "arm-off" intermediate in the intermediate- and fast-exchange regions would not qualitatively affect the spectra.[17] While this intermediate is undoubtedly present at low temperatures, it is not present in significant concentration near room temperature, as shown by (1) the relative areas of the free-dmpe and chelated-dmpe resonances, (2) equilibrium considerations (vide infra), and (3) solution molecular weight measurements. The cryoscopic molecular weight of **2** in benzene was found to be 280 ± 57. On the assumption that **2** is entirely dissociated, the number-average molecular weight for the three-particle system on the right-hand side of eq 3 is 282.

The equilibrium proposed in eq 3 also accounts for the temperature dependence of the color of solutions of **2**. Solid **2** is isolated as dark brown crystals which crush to a yellow powder. Hexane or toluene solutions of **2** are purple at room temperature and brown at −78 °C, reflecting the relative abundance of purple **3** and brown **2**.

The equilibrium constant for eq 3 can be *estimated* from the NMR data, assuming the concentration of the "arm-off" intermediate in eq 4 is zero, i.e., with the assumption that the only species present are those in eq 3. In the fast-exchange region the frequency of the signal representing dmpe exchanging between free and bridging sites (ν_{app}) is given by

$$\nu_{app} = \chi_{dmpe}\nu_{dmpe} + \chi_2\nu_2 \quad (5)$$

Table I. Equilibrium Constants[a] for the Dissociation of $Zr(\eta\text{-}C_4H_6)_2(dmpe)L$[b]

	L			
T,[c] K	$P(OMe)_3$	PMe_3	PMe_2Ph	dmpe[d]
293.7		1.63		
284.5		0.91		1.71
283.6			7.05	
279.9		0.69		
275.3		0.51		0.74
274.4			6.60	
266.1	9.05	0.35	5.58	0.37
261.5		0.28		
256.9	5.87	0.21	4.26	0.18
247.7	4.40			0.11
238.5	3.45			

[a] The principal source of error is the extrapolation of the frequency of complexed L to the appropriate temperature, which is difficult to quantify; K is estimated accurate to within 10%. [b] Measured in 70/30 toluene-d_8/THF (v/v). [c] ±2 K. [d] For dissociation of dmpe from dimeric **2** as in eq 3. These values are only approximations, as they neglect stepwise dissociation of dmpe as in eq 4 (see text).

where χ_{dmpe} and χ_2 represent the mole fractions of uncomplexed dmpe and **2** and ν_{dmpe} and ν_2 are the frequencies of uncomplexed dmpe and bridging dmpe in **2** from the limiting slow-exchange spectra. As

$$\chi_{dmpe} + \chi_2 = 1 \quad (6)$$

$$\chi_2 = (\nu_{app} - \nu_{dmpe})/(\nu_2 - \nu_{dmpe}) \equiv \theta \quad (7)$$

and

$$\chi_2 = [\mathbf{2}]/([\mathbf{2}] + [dmpe]) = [\mathbf{2}]/[\mathbf{2}]_{init} \quad (8)$$

so

$$[\mathbf{2}] = [\mathbf{2}]_{init}\theta$$

where $[\mathbf{2}]_{init}$ represents the initial concentration of **2**. At equilibrium

$$K = [\mathbf{3}]^2[dmpe]/[\mathbf{2}] \quad (9)$$

and, since the initial concentrations of dmpe and **3** are zero

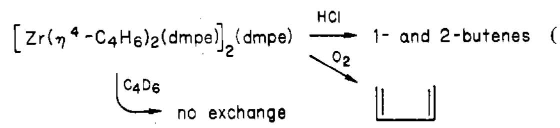
$$K = 4[dmpe]^3/[\mathbf{2}] = 4([\mathbf{2}]_{init} - [\mathbf{2}])^2/[\mathbf{2}] \quad (10)$$

so

$$K = 4[\mathbf{2}]_{init}^2(1 - \theta)^3/\theta \quad (11)$$

In practice, ν_{app} was measured at the temperature of interest; ν_2 and ν_{dmpe} were measured at several temperatures in the slow-exchange region and extrapolated to the appropriate temperature by fitting the small inherent temperature dependence of ν_2 and ν_{dmpe} to straight lines. A correction was applied to account for temperature dependence of $[\mathbf{2}]_{init}$ because of the solution volume dependence on temperature. The equilibrium constants are collected in Table I and the equilibrium thermodynamic parameters are tabulated in Table II. While only approximate because of the neglect of stepwise dissociation, the thermodynamic parameters do confirm that eq 3 is an adequate model near room temperature. If the equilibria associated with K_1 and K_2 in eq 4 each had ΔH = 5.5 kcal/mol and ΔS = 20 cal/(mol K) (half the values for eq 3), then K_1 and K_2 would be 2.17 mol/L at 298 K; a solution having an initial concentration of **2** of 0.1 M would contain 91% of its Zr as **3**, 8% as the "arm-off" intermediate, and 1% as dimeric **2**.

The presence of a Zr–H unit in **2** or as an equilibrating component in solutions of **2** is eliminated by the chemical data in eq 12. Treatment with HCl affords only butenes; no H_2 is formed. Moreover, butadiene-d_6 does not exchange with the butadiene units in **2** or exchange deuterons to any



(12)

measurable extent after 10 h at 25 °C, as determined by ^1H NMR.

Reversible CO Binding. $Zr(\eta\text{-}C_4H_6)_2(CO)(dmpe)$. Inasmuch as the fragment $Zr(C_4H_6)_2(dmpe)$ forms a stable adduct with dmpe at low temperatures, other Lewis bases should be capable of adduct formation. Solutions of **2** and excess PMe_3 are purple at room temperature and deep brown at −78 °C. At low temperatures a new ABX pattern and liberated dmpe is observed in the ^{31}P NMR of these solutions. The relative intensities of resonances attributable to complexed and uncomplexed dmpe are consistent with the equilibrium proposed in eq 13. Addition of hexane to cold solutions of **4**, formed

$$[Zr(\eta\text{-}C_4H_6)_2(dmpe)]_2(dmpe) + 2PMe_3 \rightleftharpoons dmpe + 2\underset{\mathbf{4}}{Zr(C_4H_6)_2(dmpe)(PMe_3)} \quad (13)$$

in situ from **2** and PMe_3, precipitates only the less soluble **2**. Addition of a very large excess of PMe_3 (10 equiv) forces the equilibrium in eq 13 to the right; these solutions are brown at room temperature, indicating **4** is the predominant component. However, the rate of ligand exchange is unaffected and only the least soluble component, **2**, can be isolated. Moreover, **4** is unstable at 25 °C (vide infra).

Stirring solutions or suspensions of **2** in toluene at −45 °C under 1 atm of CO results in consumption of 1 equiv of CO and formation of a yellow precipitate. When these mixtures are warmed to temperatures above −22 °C under vacuum, the consumed CO is liberated, the precipitate dissolves, and the solution turns purple. Thus, the carbonyl adduct $Zr(C_4H_6)_2(dmpe)(CO)$ (**5**) is formed reversibly, as in eq 14. The

$$[Zr(\eta\text{-}C_4H_6)_2(dmpe)]_2(dmpe) + 2CO \underset{-22\ °C,\ vacuum}{\overset{-45\ °C,\ 1\ atm}{\rightleftharpoons}} 2\underset{\mathbf{5}}{Zr(C_4H_6)_2(dmpe)(CO)} + dmpe \quad (14)$$

adduct **5** was characterized by ^{31}P and ^{13}C NMR measurements on a sample prepared in situ by using 90% enriched ^{13}CO.

The ^{13}C NMR data, collected in Table III, show a resonance with a chemical shift typical of those found for metal carbonyls.[18] Further, the signal is coupled to ^{31}P and the value of $^2J(^{13}C\text{–}Zr\text{–}^{31}P)$ is identical within the digital resolution of the spectrometer to the value measured from ^{31}P NMR spectra. ^{31}P NMR spectra indicate complexed and free dmpe in the 2:1 ratio required by eq 14.

Complex **5** is only sparingly soluble in toluene at −78 °C; consequently, it can be isolated by low-temperature filtration. The yellow, pyrophoric solid is stable at −20 °C under an atmosphere of CO or at −78 °C under vacuum. The solid may be handled for *brief* periods at 25 °C under CO but decomposes violently after several minutes at room temperature. A Zr analysis on an isolated sample of **5** further supports its formulation. When stirred at 25 °C under 1 atm of CO, solutions of **5** slowly deposit an insoluble precipitate while absorbing additional CO (up to 1.8 equiv/equiv of **5**). However, toluene solutions of **5** are stable under vacuum at temperatures up to −22 °C; at higher temperatures CO is stoichiometrically evolved and **3** is formed (eq 15).

$$Zr(C_4H_6)_2(CO)(dmpe) \xrightarrow[toluene]{-20\ to\ 0\ °C} \underset{\mathbf{3}}{Zr(\eta\text{-}C_4H_6)_2(dmpe)} + CO \quad (15)$$

Isolated **3** is a purple, crystalline solid. In contrast to **2**, solutions of **3** remain purple at low temperatures and exhibit a single ^{31}P resonance at −100 °C.

Table II. Thermodynamic Parameters for the Dissociation of $Zr(\eta\text{-}C_4H_6)_2(dmpe)L^a$

	L			
	$P(OMe)_3$	PMe_3	PMe_2Ph	dmpe^b
$\Delta H^{c,d}$	4.3 ± 0.5	8.0 ± 0.4	2.8 ± 0.5	10.9 ± 0.8
$\Delta S^{c,e}$	20.4 ± 2.0	28.0 ± 1.6	13.7 ± 1.8	39.5 ± 3.1

^{a} For reaction in 70/30 toluene-d_8/THF (v/v). ^{b} Dissociation of dmpe from dimeric **2** as in eq 3. These values are only approximations, as they neglect stepwise dissociation of dmpe (see text). ^{c} Errors are the standard errors from least-squares fits. ^{d} kcal/mol. ^{e} cal/(mol K).

Lewis Base Adducts of $Zr(\eta\text{-}C_4H_6)_2(dmpe)$. Treating coordinatively unsaturated **3** with dmpe regenerates **2**. Other tertiary phosphines react similarly. Thus, solutions of **3** and PMe_3, $P(OMe)_3$, and PMe_2Ph are brown at −78 °C and purple at 25 °C, suggesting formation of entropically disfavored adducts at low temperatures, as in eq 16. Although the

$$\underset{brown}{Zr(\eta\text{-}C_4H_6)_2(dmpe)L} \underset{-80\ °C}{\overset{25\ °C}{\rightleftharpoons}} \underset{purple}{Zr(\eta\text{-}C_4H_6)_2(dmpe)} + L \quad (16)$$

4, L = PMe_3
6, L = PMe_2Ph
7, L = $P(OMe)_3$

adducts **4**, **6**, and **7** precipitate as brown crystalline solids from concentrated toluene solutions at −80 °C, they are thermally unstable and cannot be isolated at room temperature. They can, however, be observed at low temperatures by ^{31}P NMR spectroscopy. The NMR data in Table III are consistent with an ABX pattern at −100 °C in each case. At higher temperatures, any observed ^{31}P coupling collapses and the X resonance moves to higher field, approaching and averaging with the free-ligand resonance. Simultaneously, the A and B parts average and approach the frequency of the 16-electron species **3**. Thus, at room temperature the equilibria in eq 16 are shifted to the right and the exchange rate is fast. At ∼−100 °C, ligand exchange is quenched and the equilibrium has shifted to the left. The limiting spectrum observed for **4** is identical with that obtained from solutions of **2** and PMe_3 at low temperatures, further supporting the equilibrium proposed in eq 13. By arguments similar to those in eq 5–11, it can be shown that K, the equilibrium constant for eq 16, is given by

$$K = (1 - \theta)^2[\mathbf{4}]_{init}/\theta \quad (17)$$

where

$$\theta = (\nu_{app} - \nu_L)/(\nu_{adduct} - \nu_L) \quad (18)$$

and ν_{app}, ν_L, and ν_{adduct} represent the frequencies, respectively, of the resonances associated with the exchanging L and coordinated L from the fast-exchange spectra, free ligand, and coordinated L (i.e., the X part of the ABX pattern) from spectra in the slow-exchange region. As described above, ν_L and ν_{adduct} were corrected for their inherent chemical shift dependence on temperature. Equilibrium constants at various temperatures for **4**, **6**, and **8** are collected in Table I; thermodynamic parameters from plots of ln K vs. $1/T$ are presented in Table II.

Two trends are discernible from the magnitude of ΔH for reaction 16. The size of L is critical; thus, PMe_3, $P(OMe)_3$, and dmpe with cone angles 118, 107, and 107°, respectively,[19] have comparable enthalpies of reaction. The parameters for L = dmpe are, however, only approximations because of neglect of stepwise dissociation. Formation of the adduct **6**, is less exothermic, as expected for larger PMe_2Ph (cone angle 122°[19]). Indeed, triphenylphosphine does not form a detectable

Table III. ^{31}P and ^{13}C NMR Data[f] for $Zr(\eta\text{-}C_4H_6)_2$(dmpe) and Its Lewis Base Adducts[a,b]

compd (*T*, K)	A		B	X
$Zr(\eta\text{-}C_4H_6)_2$(dmpe)[c] (300)	10.1			
$Zr(\eta\text{-}C_4H_6)_2$(dmpe)[$P(OMe)_3$][d] (183)	−3.3		9.1	174.8
	J_{AX} = 24.3		J_{BX} < 1.2	J_{AX} = 24.3
		J_{AB} < 1.2		
$Zr(\eta\text{-}C_4H_6)_2$(dmpe)(^{13}CO)[d] (228)	33.6		−16.6	247.6[e]
	J_{AX} = 12.8		J_{BX} < 0.6	J_{AX} = 12.5
		J_{AB} ≤ 0.6		
$Zr(\eta\text{-}C_4H_6)_2$(dmpe)(PMe_2Ph)[d] (183)	−1.7		−9.8	12.3
	J_{AX} = 9.8		J_{BX} = 9.8	$J_{AX} \simeq J_{BX}$ = 9.8
		J_{AB} = 36.6		
$Zr(\eta\text{-}C_4H_6)_2$(dmpe)(PMe_3)[d] (183)	−8.3		−10.0	10.3
	J_{AX} = 9.8		J_{BX} = 9.8	$J_{AX} \simeq J_{BX}$ = 9.8
		J_{AB} = 3.3		
[$Zr(\eta\text{-}C_4H_6)_2$(dmpe)]$_2$(dmpe)[d,g] (183)	−1.2		−10.3	10.7

[a] Chemical shifts are in parts per million; coupling constants are in hertz. [b] ^{31}P data are relative to 85% H_3PO_4 and ^{13}C data are relative to Me_4Si; a resonance at higher field than the reference is negative. [c] In benzene-d_6, a singlet. [d] In 70/30 toluene-d_8/THF (v/v). [e] ^{13}C resonance of Zr–^{13}CO unit. [f] Only the absolute values of J_{PP} are given. [g] ^{31}P coupling unresolved.

Table IV. Comparative ^{13}C NMR Data[a] for $Zr(\eta\text{-}C_4H_6)_2$(dmpe)

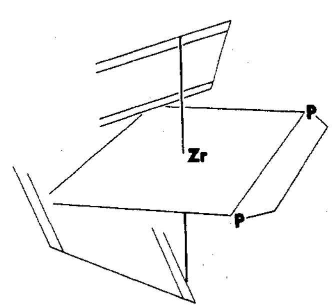
compd	$\delta(C_{1,4})$ (J_{CH}, Hz)	$\delta(C_{2,3})$ (J_{CH}, Hz)
butadiene[30b,35,36]	117.5 (158)	137.7 (158)
$Fe(\eta\text{-}C_4H_6)(CO)_3$[30b,35,36]	40.4 (160.6)	85.2 (168.7)
Fe(η-cyclohexadiene)$(CO)_3$[36]	62.5 (158.2)	85.4 (172.8)
$Ti(\eta\text{-}C_5H_5)(\eta$-methallyl)-($\eta\text{-}C_4H_6$)[9b]	61.4, 58.5 (155)[b]	114.2 (160)
$Zr(\eta\text{-}C_4H_6)_2$(dmpe)	39.1 (146)	105.6 (156)
sp^3 CH[37]	(125–130)[c]	
sp^2 CH[37]	(156–171)[c]	

[a] Chemical shifts are in parts per million, relative to Me_4Si; coupling constants are in hertz. [b] In this complex the ends of the butadiene ligand are measurably chemically inequivalent. [c] Typical ranges for J_{CH}.

adduct with **3** at −100 °C. Although the data are limited, it would appear that the complex **3** prefers σ-donor capabilities to π acidity in L; thus, $P(OMe)_3$, a smaller ligand than PMe_3, binds **3** less exothermically. Trimethyl phosphite is generally regarded a better π acceptor and poorer σ donor than PMe_3.[20] Indeed, although **3** forms a moderately stable carbonyl adduct, no ethylene adduct could be detected by ^{31}P NMR at temperatures as low as −110 °C. Complex **3** was irreversibly decomposed by PF_3.

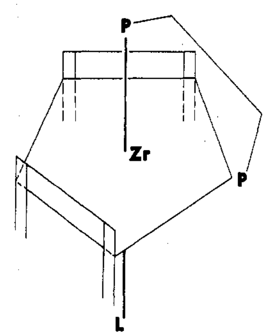
Finally, we note that **2** is thermodynamically unstable at room temperature with respect to **3** and free dmpe. The dimer **2** can be isolated only because the bidentate nature of the Lewis base makes complete dissociation and volatilization of dmpe slow in the solid state. Heating **2** to 100–150 °C under vacuum results in liberation of dmpe and sublimation of **3**. This is not a useful method for preparing **3**, as considerable decomposition accompanies its volatilization.

Structural Features and the Nature of the Butadiene Ligand. The chemical equivalence of the dmpe chelate ends from ^{31}P NMR data and of the butadiene carbon atoms from ^{13}C NMR data (Table IV) are consistent with a C_2 structure for **3**, based on a distorted octahedron.



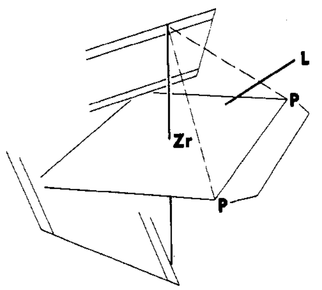
This structure requires that the ^{13}C NMR resonances of C_1 and C_4 of each butadiene group either be accidentally degenerate or undergo exchange by an undefined mechanism. Additionally, the endo isomer obtained by rotating each butadiene group so as to place the C_4H_6 backbones nearest the C_2 axis equally well accommodates the data.

The spectral data do not allow unambiguous structural assignments for the seven-coordinate adducts **2**, **4**, **5**, **6**, and **7**. The ^{31}P NMR spectral parameters do, however, suggest that two different structures may occur, depending on the nature of the Lewis base. The ^{13}C-labeled carbonyl adduct **5** has ^{13}C and ^{31}P NMR spectra (Table III) consistent with an ABX spin system for the $Zr^{31}P_2{}^{13}CO$ fragment with J_{AX} = 12.5 Hz and $J_{BX} = J_{AB} \leq 0.6$ Hz. Inasmuch as $^2J(^{31}P\text{–}M\text{–}^{13}C)$ for a trans arrangement is generally larger than that for a cis arrangement (on the basis of trends observed for group 6 and 7 carbonyl–phosphine complexes[18,21]), the observed couplings suggest a structure with an approximately linear P–Zr–^{13}CO unit, the remaining end of the chelating phosphine occupying a site cis to the carbonyl group. The requisite structural features can be accommodated by, but do not prove, a geometry based on a pentagonal bipyramid. The low-field



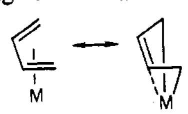
chemical shift of the phosphorus atom most strongly coupled to the ^{13}CO ligand may reflect its location trans to the carbonyl group.[22] Although the $P(OMe)_3$ adduct **5** has a substantially smaller chemical shift difference between the ends of the dmpe chelate, it has similar ^{31}P coupling constants; i.e., J_{AX} is large while $J_{AB} \simeq J_{BX} \simeq 0$. As $^2J(^{31}P\text{–}M\text{–}^{31}P)$ for trans structures is generally larger than those for cis structures,[23] **5**, likely, has a similar Zr(dmpe)L arrangement. The data may also be accommodated by a pentagonal-bipyramidal structure. The poor solubility of **5** and **7** at low temperatures precludes observation of ^{13}C resonances (other than that from the ^{13}C-enriched carbonyl group of **7**). In the absence of additional spectroscopic data, it is not possible to uniquely specify a geometry. Any structure for **5** and **7** having L trans to one end of the dmpe chelate is allowed.

In contrast to **5** and **7**, the PMe_3 and PMe_2Ph adducts have $J_{AX} \simeq J_{BX}$ (where the X resonance corresponds to that for PMe_3 or PMe_2Ph), implying a different Zr(dmpe)L arrangement. It is possible to accommodate these data with a number of structures based on the idealized seven-coordinate geometries.[24] A possible structure, based on a monocapped octahedron and requiring minimum rearrangement of **3**, is shown below. This C_1 structure is consistent with the small chemical shift difference between the ends of the dmpe chelate in the PMe_3 adduct **4**. The larger chemical shift differences in **2** and **6** may reflect additional distortion.



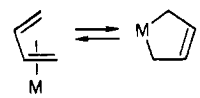
It should be noted that the enthalpies for dissociation of L from adducts of **3** (Table II) are the sums of the enthalpies for rearrangement of **3** and of the enthalpies for Zr–L bond formation. The Zr–L bond may be substantially stronger than implied by the small ΔH values for the equilibria in eq 14 and 16.

Butadiene complexes are generally described as resonance hybrids of the limiting forms A and B. Form A represents



A B

a bonding mode involving, principally, the filled π levels of butadiene; form B reflects substantial occupation of the LUMO of butadiene.[25] The relative weighting of these forms, i.e., the degree of occupation of the ψ_3 orbital of the butadiene ligand, is reflected by particular structural features, e.g., the relative C_1–C_2 and C_2–C_3 bond lengths and the bond angles associated with the disposition of substituents about C_4, implying sp^3 or sp^2 character.[25,26] It is also conceivable that a particular butadiene complex might exist as a mixture of equilibrating *isomers* involving a metallocyclopentene complex, as in eq 19. The metallocyclopentene isomer differs struc-



(19)

turally from resonance hybrids of A and B in that C_2 and C_3 are not significantly bound to the metal. Related equilibria have been inferred for bis(ethylene) complexes of Ti(II),[27] Ni(0),[28] and Ta(III).[29] Since low-valent group 4 complexes appear to be powerful reductants,[6,10,27] it is attractive to suppose that complex **3**, for example, may be a zirconium(IV)–bis(metallocyclopentene) complex or have a structure which reflects an abnormal weighting of resonance form B.

The ^1H chemical shifts of the butadiene protons of **3** are very similar to those for $(\eta$-$C_4H_6)Fe(CO)_3$,[30] eliminating the possibility of a metallocyclopentene form. The ^{13}C chemical shifts and J_{CH} values are compared with those for butadiene and other diene complexes in Table IV. In particular, J_{CH} for C_1 and C_4 is 9% lower in **3** than in $Fe(\eta$-$C_4H_6)(CO)_3$, 6% lower than in the Ti(II) complex $Ti(\eta$-$C_5H_5)(\eta$-methallyl$)(\eta$-$C_4H_6)$, and 8% lower than in butadiene. The observed coupling is intermediate between typical sp^3 and sp^2 J_{CH} values. This suggests that, although **3** is similar to $Fe(\eta$-$C_4H_6)(CO)_3$ and the Ti(II)–butadiene complex, its structure may reflect an increased weighting of resonance form B. This is consistent with the notion that the ZrP_2 fragment is a powerful electron donor.

Table V. Rate Constants for Hydrogenation of Olefins, Using $[Zr(\eta$-$C_4H_6)_2(dmpe)]_2(dmpe)$ as a Catalyst

substrate	10^3k,[a] min^{-1}	conditions[b]	$k' = k/[Zr]$,[c] $M^{-1}\ min^{-1}$
1-octene	1.79 ± 0.02	$p(H_2) = 770$ mm, $[Zr] = 2.34 \times 10^{-2}$ M	7.65×10^{-2}
cyclohexene	1.29 ± 0.02	$p(H_2) = 774$ mm, $[Zr] = 1.46 \times 10^{-2}$ M	8.84×10^{-2}
2-pentyne[d]	3.13 ± 0.22	$p(H_2) = 767$ mm, $[Zr] = 1.7 \times 10^{-2}$ M	1.84×10^{-1}
2-methyl-2-butene	no reaction		

[a] First-order rate constant; error limits are standard errors from least-square fits. [b] $T = 25.0 \pm 0.2$ °C in all cases. [c] First-order dependence on Zr assumed. [d] *cis*-2-Pentene was the initial reduction product, as determined by GLC monitoring of the reaction.

Poor solubility at low temperatures precluded observation of the ^{13}C NMR resonances of the butadiene carbons in the seven-coordinate adducts **2**, **4**, **5**, **6**, and **7**. However, the ^1H NMR resonances of **2** at −80 °C are not significantly shifted from those for **3** and no structural changes in the $Zr(\eta$-$C_4H_6)_2$ unit are indicated.

Hydrogenation of Olefins. Solutions of **2** and **3** react rapidly with H_2 at 1 atm and 25 °C, liberating butane and depositing (in alkane solvents) a Zr mirror on the walls of the reaction vessel. In benzene or toluene and in the presence of an olefin, brown solutions are formed which remain homogeneous. These solutions are effective catalysts for the hydrogenation of olefins and alkynes. After an initial rapid uptake, hydrogen consumption and olefin disappearance follow first-order kinetics. Rate constants for representative substrates are tabulated in Table V, as are the second-order rate constants derived by *assuming* a rate law of the form[31]

$$-d[\text{olefin}]/dt = k[\text{olefin}][\text{Zr}] \qquad (20)$$

Although **2** is an effective catalyst precursor, it is substantially slower than others; e.g., the second-order rate constants for hydrogenation of cyclohexene at 1 atm of H_2 pressure in benzene are $5.7 \times 10^3\ M^{-1}\ min^{-1}$ for $RhCl(PPh_3)_3$[32] and $8.84 \times 10^{-2}\ M^{-1}\ min^{-1}$ for **2**. Further, **2** and its derivatives are oxidized by ketones and compounds having active halogens.

Hydrogenated solutions of **2** are complex, ^{31}P NMR spectra are complex and unresolved, and small concentrations of paramagnetic species are present as shown by the presence of ESR signals.[33] Addition of butadiene to hydrogenated solutions of **2** does not regenerate **2** or **3**. The actual species functioning as a hydrogenation catalyst is unknown; it seems likely that the small rate constants reflect only the presence of a small concentration of the active species.

Conclusions

Under mild conditions the 16-electron $Zr(\eta$-$C_4H_6)_2(dmpe)$ fragment is both stable and inert. Thus, ligand exchange between complexed bidentate and free dmpe or between complexed and free butadiene is not detectable. This behavior is a probable consequence of the balance between π-accepting and σ-donating ligands. Although **3** and related derivatives formally contain Zr(0), the significant population of the LUMO of butadiene reflected by the $J_{^{13}CH}$ values of the terminal, methylene carbons of the ligand suggests substantial transfer of electron density from zirconium. This hypothesis is supported by the observation that **3** functions as a Lewis acid, forming weakly bound adducts with CO and small tertiary phosphines and phosphites.

Complex **3** does not insert into C–H bonds. For example, the central metal does not insert into the methyl groups of dmpe, as does occur with Ru,[34] Ir,[3] and Fe[1c] complexes of methylated phosphines. It is likely that increased phosphine substitution and less effective π-accepting ligands than butadiene are necessary to enhance this type of reactivity.

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Registry No. **1**, 69859-75-2; **2**, 69878-77-9; **3**, 71328-76-2; **4**, 69891-40-3; **5**, 71328-72-8; **6**, 71328-73-9; **7**, 71359-29-0; 1-octene, 111-66-0; cyclohexene, 110-83-8; *cis*-2-pentene, 627-20-3; $ZrCl_4$, 10026-11-6.

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Synthesis of Macrocyclic Complexes of Gold(III) by Condensation of Bis(ethylenediamine)gold(III) Chloride with β-Diketones

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Bis(ethylenediamine)gold(III) chloride in aqueous base reacts with a variety of β-diketones via Schiff base condensation to form 14-membered, tetraaza ring, 12π macrocyclic complexes of gold(III). Reaction intermediates in which condensation of only one β-diketone has occurred can be isolated and condensed with a different β-diketone to provide variety in substituents on the macrocyclic ring. Oxidation of (5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenato)gold(III) hexafluorophosphate, I, with trityl tetrafluoroborate introduces a double bond in one of the five-membered rings. Gold can be removed from macrocycle I by reduction with Zn in aqueous base, and the free ligand so obtained may be used to prepare macrocyclic complexes of other metal ions. No condensation products could be isolated upon treating $[Au(en)_2]Cl_3$ in aqueous base with 1,1,1,5,5,5-hexafluoropentane-2,4-dione, 2,2,6,6-tetramethylheptane-3,5-dione, biacetyl, biguanide, acetone, or 1,1,3,3-tetramethoxypropane.

Efforts by several investigators during the past few years have shown that amine ligands bound to Pt(IV), Ru(II) and -(III), and Os(III) are readily deprotonated in aqueous base and that the resulting coordinated amides show nucleophilic behavior toward certain carbonyl-containing substrates.[1-6] For example, one or more β-diiminate chelate rings are formed when $Pt(NH_3)_6^{4+}$ and $Pt(en)_3^{4+}$ are treated with 2,4-pentanedione in aqueous base.[3] A crystallographic study of one

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