Acknowledgment. The authors wish to thank the National Research Council (CNR, Rome) for support.

Registry No. $Pd_2Cl_4(CO)_2$, 75991-68-3; $Pt_2Cl_4(CO)_2$, 17522-99-5; $NH_2Et_2[PdCl_3(CO)]$, 75934-65-5; $[PtCl_3(CO)]^-$, 21710-57-6; $PdCl_2$, 7647-10-1; $PtCl_2(CO)_2$, 15020-32-3.

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Preparation of Tertiary Phosphine–Olefin Complexes of Platinum(0): A Convenient Synthesis of Ethylenebis(triethylphosphine)platinum(0)[1]

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Presently available synthetic routes to complexes of trialkylphosphines with platinum(0) involve starting materials which are not readily available,[4–6] difficult isolations,[7] and manipulations of air-sensitive materials.[4–8] The more convenient of these preparations entail displacement of cyclooctadiene from bis(cyclooctadiene)platinum(0), but this compound is prepared only in moderate yield (40–60%) by an inconvenient reaction.[9] One of the simplest members of the class of platinum(0)–phosphine complexes, ethylenebis(triethylphosphine)platinum(0) (**1**) has not been reported. We wish to report a convenient, high-yield preparation of **1** by thermal decomposition of the air-stable, crystalline complex diethylbis(triethylphosphine)platinum(II). The generality of this thermal decomposition reaction as a route to platinum(0)–phosphine complexes is examined briefly.

Experimental Section

General Information. Proton NMR spectra were recorded on a Bruker WM-250 instrument. $\{^1H\}^{31}P$ NMR spectra were obtained at 36.4 MHz on a modified Bruker HFX-90 or Jeol FX-90Q spectrometer. ^{31}P chemical shifts, in parts per million, are relative to external 85% phosphoric acid (downfield shifts positive). Mass spectra were recorded on a Varian MAT-44 spectrometer. Olefins were removed from cyclohexane by treatment with concentrated H_2SO_4, and the cyclohexane was washed with saturated $NaHCO_3$, dried over P_4O_{10}, and distilled under argon. Toluene-d_8 was passed through a 1 × 2 cm column of activated alumina and degassed by freeze–pump–thaw cycles. Ether was distilled under argon from sodium benzophenone dianion. Welding grade argon was used for inert-atmosphere work without further purification. Compounds were stored in a dessicator at −10 °C.

Diethyl- and dipropylbis(triethylphosphine)platinum(II) were prepared by modifications of literature methods.[10,11]

Dicyclobutylbis(triethylphosphine)platinum(II). Special care was needed in preparing the thermally unstable dicyclobutyl and dicyclopentyl compounds. In an argon-flushed 100-mL flask was suspended 0.50 g (1.3 mmol) of dichloro(1,5-cyclooctadiene)platinum(II)[10] ((COD)$PtCl_2$) in 40 mL of ether. To this mixture was added 10 mL of 0.53 M (5.3 mmol) cyclobutylmagnesium chloride by syringe at −50 °C. The solution was allowed to warm to −20 °C over 2 h and stirred at this temperature for 6 h. The entire reaction mixture was passed through a 1 × 6 cm column of silica gel containing 5% activated charcoal at −78 °C. The solution thus obtained was treated with 0.40 mL (2.8 mmol) of triethylphosphine at 0 °C. After 15 min the ether was partially removed under reduced pressure. Adding methanol (5 mL) and cooling to −78 °C induced crystallization. The white precipitate was separated by filtration and recrystallized from ether–methanol to give 0.40 g (56%) of fine needles, mp 87–88 °C. ^{31}P NMR: $\delta = 6.3$ ($J_{Pt,P} = 1647$ Hz).

Table I. Platinum(0) Complexes Prepared by Thermal Decomposition of $L_2Pt^{II}R_2$

complex	dec temp, °C (*t*, h)	yield, %	$\delta(^{31}P)$	$J_{Pt,P}$, Hz
$(Et_3P)_2Pt$(ethylene)^a	118 (0.5)	100^c	20.6	3551
$(Me_3P)_2Pt$(ethylene)^b	118 (1.2)	$>70^d$	$-19.5^{e,f}$	$3435^{e,f}$
$(Et_3P)_2Pt$(propylene)^a	80 (10.0)	$>80^d$	21.1, 18.5	3767, 3279^g
$(Et_3P)_2Pt$(cyclobutene)^a	40 (4.0)	95^d	20.1	3418
$(Et_3P)_2Pt$(cyclopentene)^a	35 (1.0)	75^c	*e*	*e*
$(Ph_3P)_2Pt$(cyclobutene)^b	35 (0.5)	40^d	34.2	3604
$(DMPE)_2Pt^b$	182 (20.0)	95^d	−8.1	3724

^{a} Cyclohexane was the solvent for decompositions. ^{b} Toluene was the solvent for decompositions. ^{c} Determined by treatment with methyl iodide. ^{d} Estimated from NMR peak heights. ^{e} Rapid exchange of R_3P groups was observed in the ^{31}P NMR spectrum at room temperature. ^{f} At −45 °C. ^{g} $J_{P,P} = 66$ Hz.

Dicyclobutylbis(triphenylphosphine)platinum(II). This compound was prepared by a procedure similar to that described for the triethylphosphine complex except as noted. Triphenylphosphine was added to the solution of (COD)$Pt(C_4H_7)_2$ as a solution in a minimum volume of diethyl ether at 0 °C. The product precipitated directly from the ether solution without addition of methanol, giving 0.42 g (41%) of white needles, mp 87–97 °C dec. ^{31}P NMR: $\delta = 26.3$ ($J_{Pt,P} = 1709$ Hz).

Dicyclopentylbis(triethylphosphine)platinum(II). In a 250-mL round-bottomed flask was placed 0.50 g (1.3 mmol) of (COD)$PtCl_2$. The flask was fitted with a stirring bar, sealed with a rubber septum, and flushed thoroughly with argon. Into the flask was transferred 100 mL of ether via cannula, and the mixture was cooled to −50 °C. To the stirred mixture was added by syringe 10.0 mL of 0.60 M cyclopentylmagnesium bromide in THF. The reaction mixture was stirred vigorously at −50 °C for 4 h, warmed slowly to −20 °C, and stirred for an additional 4 h. The reaction was quenched by addition of 10 mL of 20% methanol in water by syringe. The ether layer was decanted via cannula into a 100-mL flask and the ether removed at −20 °C under reduced pressure to a volume of ca. 10 mL. Cold methanol (30 mL) containing 1.00 mL (0.810 g, 6.86 mmol) of triethylphosphine was added to this solution. The solution was stirred for 3 h at −20 °C during which time a white crystalline solid precipitated. The solution was further concentrated at reduced pressure, cooled to −30 °C, and filtered rapidly on a coarse frit. The product was washed with two 3-mL portions of cold (−30 °C) methanol and dried in vacuo to give an off-white solid in 43% overall yield; mp 59–61 °C dec. ^{31}P NMR: $\delta = 9.0$ ($J_{Pt,P} = 1616$ Hz).

General Decomposition Procedure. Thermal decompositions of diethyl- and dipropylplatinum(II) complexes were carried out in sealed tubes by procedures analogous to that described below for the preparation of ethylenebis(triethylphosphine)platinum(0). Indistinguishable results have been obtained in serum-capped tubes under argon.[12] Cyclobutyl and cyclopentyl complexes were decomposed in serum-stopped test tubes under an argon atmosphere. ^{31}P NMR data for all new platinum(0) complexes are in Table I. Yields of platinum(0) complexes were determined either by measuring the yield of iodomethylbis(phosphine)platinum(II) obtained after reaction with methyl iodide or by estimating ^{31}P NMR peak heights relative to triethylphosphate internal standard. Comparable results were obtained by either method.

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(3) National Science Foundation Predoctoral Fellow, 1978–1981.
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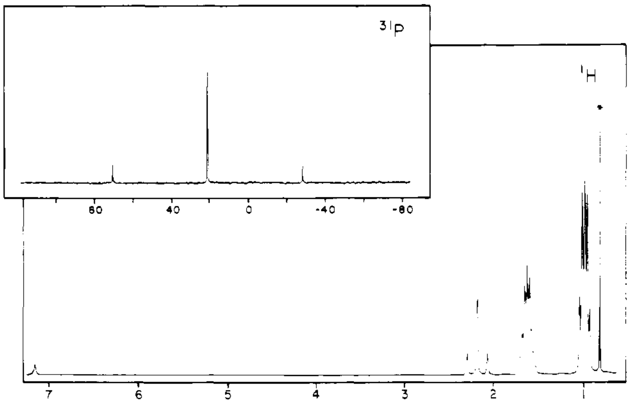


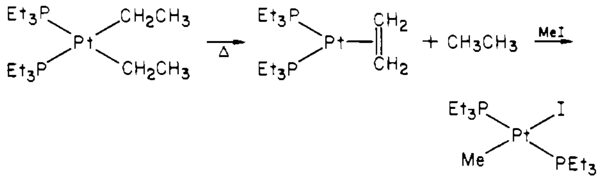
Figure 1. Ambient-temperature $\{^1H\}^{31}P$ and 250-MHz ^1H NMR spectra of (ethylene)bis(triethylphosphine)platinum(0) produced by thermal decomposition of diethylbis(triethylphosphine)platinum(II) in benzene-d_6 at 118 °C. The asterisk denotes ethane; the triplet at $\delta = 2.2$ is due to coordinated ethylene.

(Ethylene)bis(triethylphosphine)platinum(0). Diethylbis(triethylphosphine)platinum(II) (100 mg, 0.204 mmol) was placed in a clean, dry, Pyrex tube which was then evacuated to 0.1 torr and flushed with argon: NMR tubes were used for much of this work. Dry, degassed cyclohexane (1 mL) was introduced by syringe. The tube was cooled (liquid nitrogen), evacuated (0.1 torr), sealed, allowed to warm to room temperature, and heated at 118 °C (oil bath) for 30 min. The resulting solution contained $(Et_3P)_2Pt^0C_2H_4$ as the only detectable phosphorus-containing species (Figure 1). The ^1H NMR spectrum exhibits a single set of resonances for platinum-coordinated ethylene ($\delta = 2.15$ ($J_{Pt,H} = 55$ Hz)); free ethylene is not observed.

Reaction of $(Et_3P)_2Pt^0C_2H_4$ with Methyl Iodide. The tube was opened in an argon stream and treated with 0.1 mL (excess) of methyl iodide. After ca. 30 min the contents of the tube were poured onto a watch glass. Evaporation of the solvent and excess methyl iodide yielded 116.7 mg (100%) of off-white *trans*-iodomethylbis(triethylphosphine)platinum(II), identified by its melting point of 68–71 °C (lit.[13] mp 71.0–71.5 °C), mass spectrum (m/e 573 $[M]^+$), and ^{31}P NMR spectrum (cyclohexane) [$\delta = 10.1$ ($J_{Pt,P} = 2778$ Hz), lit.[14] $\delta = 9.4$ ($J_{Pt,P} = 2754$ Hz)].

Results and Discussion

Diethylbis(triethylphosphine)platinum(II) decomposes thermally in cyclohexane solution by β-hydrogen activation followed by reductive elimination of ethane (eq 1).[15] The



(1)

solution changes from colorless to dark orange over the course of the thermolysis. Free ethylene is not visible in the ^1H NMR spectrum; the ^{31}P and ^1H NMR spectra[16] exhibit resonances which can be attributed to ethylenebis(triethylphosphine)platinum(0) (Figure 1). The orange color is apparently due to an impurity,[17] although the solution behaves chemically and spectroscopically as though it were pure. When the solution is treated with methyl iodide, its orange color disappears, ethylene appears in the ^1H NMR spectrum, and *trans*-iodomethylbis(triethylphosphine)platinum(II) is formed in quantitative yield. Compound **1** can be isolated as a dark orange oil by solvent removal. Attempted purification by low-temperature crystallization has led to less pure oils.

The generality of this method for preparing complexes having the structure L_2Pt^0(olefin) has been explored (Table I). The procedure seems to tolerate alkyl and phosphine substitution, although the yield of (olefin)bis(phosphine)platinum(0) obtained depends on the nature of the olefin formed, the phosphine, and the temperature at which the thermolysis is carried out. (Cyclobutene)bis(triethylphosphine)platinum(0) can be prepared under the conditions described in Table I; the solution containing this compound is colorless. A labile cyclopentene complex of L_2Pt^0 can be prepared from dicyclopentylbis(triethylphosphine)platinum(II) by decomposition at ambient temperature. At higher temperatures the olefin complex decomposes. Similarly, decomposition of dipropylbis(triethylphosphine)platinum(II) at 80 °C gives the propene complex. Under the more severe conditions for formation of **1** (118 °C, Table I), this olefin complex is a minor product; the reaction solution is dark brown and contains $(Et_3P)_3Pt^0$ as a major constituent.[20] Thus, the strongly coordinating ethylene, or an equivalent olefin, seems to be necessary for the stabilization of these bis(trialkylphosphine)platinum(0) moieties at higher temperatures. Compound **1** begins to disproportionate[20] at ca. 150 °C.

Thermal decomposition of diethyl[1,2-bis(dimethylphosphino)ethane]platinum(II) does not give a stable olefin complex. (Cyclobutene)bis(triphenylphosphine)platinum(0) can be prepared by this method but is contaminated by $L_3Pt(0)$ and "LPt(0)" oligomers[17] which are significant coproducts. (Ethylene)bis(trimethylphosphine)platinum(0) forms in good yield, but, unlike **1**, rapid intermolecular exchange of phosphine moieties is indicated by the ^{31}P NMR spectrum at room temperature. We do not know if impurities are responsible for this behavior.

Thermal decomposition of L_2PtR_2 complexes in the presence of added phosphine yields tris- and tetrakis(phosphine)platinum(0) complexes. Decomposition of diethylbis(triethylphosphine)platinum(II) in the presence of 1 equiv of triethylphosphine yields a bright yellow solution which contains free ethylene. Evaporation of solvent gives $(Et_3P)_3Pt^0$ as an orange oil. Thermolysis of diethyl[1,2-bis(dimethylphosphino)ethane]platinum(II) in toluene at 182 °C in the presence of dmpe gives $(dmpe)_2Pt^0$ as the only product.

Thermal decomposition of diethylbis(triethylphosphine)platinum(II) is a convenient, high-yield preparation of compound **1**. The overall yield of **1** from dichloro(cyclooctadiene)platinum(II)[10] is 86%. As a precursor to platinum(II) compounds, **1** has the advantage over $(Et_3P)_3Pt^0$ that ethylene is the coproduct. The reaction can be used to generate other (olefin)bis(phosphine)platinum(0) complexes, but yields and purities may be lower than for **1**.

Registry No. **1**, 76136-93-1; $(Me_3P)_2Pt$(ethylene), 69547-16-6; $(Et_3P)_2Pt$(propylene), 76136-94-2; $(Et_3P)_2Pt$(cyclobutene), 76136-95-3; $(Et_3P)_2Pt$(cyclopentene), 76136-96-4; $(Ph_3P)_2Pt$(cyclobutene), 76136-97-5; $(DMPE)_2Pt$, 25398-78-1; $(Et_3P)_2PtEt_2$, 76189-28-1;

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(17) (Ethylene)bis(triphenylphosphine)platinum(0) is white;[18] the orange color may arise from an oligomerization[19] or from an equilibrium forming $(Et_3P)_{3,4}Pt^0$.

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$(Me_3P)_2PtEt_2$, 76136-98-6; $(Et_3P)_2PtPr_2$, 76189-29-2; $(Et_3P)_2Pt(C_4H_7)_2$, 76156-55-3; $(Et_3P)_2Pt(C_5H_9)_2$, 76136-99-7; $(Ph_3P)_2Pt(C_4H_7)_2$, 76137-00-3; (DMPE)$PtEt_2$, 76137-01-4; (COD)$PtCl_2$, 12080-32-9; *trans*-$(Et_3P)_2Pt(Me)I$, 18974-13-5; MeI, 74-88-4; cyclobutylmagnesium chloride, 76124-42-0; cyclopentylmagnesium bromide, 33240-34-5.

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Nickel(II) Complexes of New S_2N_2-Donor Macrocycles. Synthesis and Kinetics of Dissociation

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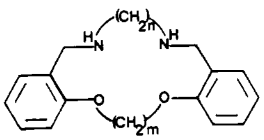
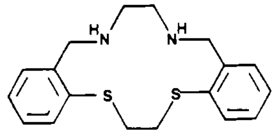
Transition-metal complexes of macrocyclic ligands incorporating N_4- and S_4-donor sets have been well investigated (especially for studies concerning the nature of the macrocyclic effect).[1] With nickel(II), the N_4 systems are usually very kinetically inert[2] (and thermodynamically stable) whereas the S_4 macrocycles yield complexes which are much more labile.[3] The metal-ion chemistry of S_2N_2 macrocycles has received less attention, and few such ligands have been reported previously.[4-6]

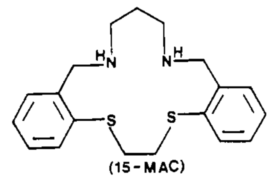
As an extension of our recent studies involving O_2N_2-donor macrocycles of type **1**,[7-9] the syntheses of the analogous S_2N_2-donor macrocycles **2**–**4** are now reported. Since thioether donors tend to have stronger affinities for nickel(II) than do ether donors, the nickel complexes of the new macrocycles might mainly be expected to exhibit labilities which fall between those of O_2N_2-donor and N_4-donor macrocyclic complexes. We present here a report of the interaction of nickel with the new 14- to 16-membered macrocycles of types **2**–**4** together with a study of the kinetics of dissociation of the nickel complex of the 15-membered ring.



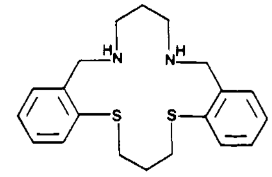
n, m = 2 or 3
1



(14-MAC)
2



(15-MAC)
3



(16-MAC)
4

Experimental Section

The instrumentation used for the physical measurements has been described previously.[7-9] Infrared spectra were obtained on Nujol mulls of the compounds, the spectrophotometer was calibrated against a polystyrene standard. ^1H and ^{13}C NMR chemical shifts are relative to tetramethylsilane (Me_4Si) for $CDCl_3$ solutions and 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) for D_2O solutions.

The kinetic study was performed in aqueous media ($I = 1.0$) under conditions identical with those described previously.[8] The dissociation was followed spectrophotometrically at 600 nm. The consecutive rate constants were obtained with the aid of a computer program described elsewhere.[10]

1,4-Bis(2-benzyl alcohol)-1,4-dithiabutane. A stirred suspension of 1,4-bis(2-carboxyphenyl)-1,4-dithiobutane (33.4 g), prepared as described previously,[11] in ether (300 mL) was slowly added to a stirred suspension of $LiAlH_4$ (8.0 g) in ether (600 mL). The mixture was refluxed under N_2 for 100 h and then cooled to 0 °C. Excess $LiAlH_4$ was destroyed by careful dropwise addition of water (8 mL), 15% NaOH (8 mL), and then water (24 mL).[12] The gelatinous white solid was filtered off and dried by mixing with an equal weight of Na_2SO_4. This mixture was then extracted several times with hot chloroform. The extracts were combined with the ether filtrate, and this was then evaporated to dryness to yield crude product which was recrystallized from chloroform to yield white needles: yield 40%; mp 111 °C; mass spectrum parent ion *m/e* 306. Anal. Calcd for $C_{16}H_{18}O_2S_2$: C, 62.7; H, 5.9. Found: C, 62.4; H, 6.1. The IR spectrum contained a broad OH stretching band in the region 3220–3320 cm^{-1}.

1,5-Bis(2-benzyl alcohol)-1,5-dithiapentane. A similar procedure to the above yielded this diol as an oil (yield 45%) which was characterized by NMR and used without further purification. ^1H NMR ($CDCl_3$): 1.89 (quintet, SCH_2CH_2), 3.01 (t, SCH_2), 4.78 (s, CH_2OH), 7.20–7.55 (m, aromatic). The IR spectrum was very similar to that of the above compound and contained a broad OH stretching band in the region 3220–3320 cm^{-1}.

1,4-Bis(2-formylphenyl)-1,4-dithiabutane. A mixture of 1,4-bis(2-benzyl alcohol)-1,4-dithiabutane (6.2 g) in ether and excess activated manganese dioxide (MnO_2—type B)[13] was refluxed for 24 h. MnO_2 was filtered off and washed several times with hot chloroform, and the wash solutions were combined with the ether filtrate. The solution was evaporated to dryness to yield the product. Recrystallization from ether gave white crystals: yield 95%; mp 136 °C (lit. 137 °C).[14] IR: $\nu_{C=O}$ 1675 cm^{-1}. ^1H NMR ($CDCl_3$): 3.10 (s, CH_2), 7.10–7.75 (m, aromatic), 10.16 (s, CHO).

1,5-Bis(2-formylphenyl)-1,5-dithiapentane. A procedure similar to the above converted the corresponding diol to the required product as white crystals after recrystallization from methanol: yield 90%; mp 56–57 °C. IR: $\nu_{C=O}$ 1675 cm^{-1}. ^1H NMR ($CDCl_3$): 2.05 (quintet, SCH_2CH_2), 3.01 (t, SCH_2), 7.12–7.83 (m, aromatic), 10.38 (s, CHO).

General Preparation for the S_2N_2-Donor Macrocycles. Diamine (1,2-diaminoethane or 1,3-diaminopropane; 0.01 mol) in dry methanol (50 mL) was slowly added to a stirred solution of the appropriate dialdehyde (0.01 mol) in dry methanol (300 mL). Borax[15] (0.5 g) and then $NaBH_4$ (1.0 g) were added, and the solution was concentrated to 80 mL. Water (300 mL) was added, and the solution was extracted with chloroform (three times). The extracts were dried over anhydrous sodium sulfate and were then added to an equal volume of dry ether. Dry HCl gas was passed through this solution, and the white solid

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