Reaction of (.pi.-allyl)palladium complexes from allene with nucleophiles. Synthesis of conjugated exocyclic dienes

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of degassed chloromethane was added by syringe. The mixture was stirred magnetically for 2 min and then stopped. An IR spectrum taken at this point showed the presence of the characteristic cumulenic absorption of the ligand 8 near 2050 cm^{-1} and the absence of the allenic absorption due to the complex (Table I). After removal of solvent and chromatography (unactivated silica, hexanes), 5.2 mg of butatriene 8 was recovered (72%). similar reactions using the other platinum complexes gave good yields of recovered butatrienes.

Attempted Binuclear Platinum Complexes. In a typical reaction, 37.4 mg (50 μmol) of complex 1 was allowed to react with 9.1 mg (25 μmol) of cumulene 8 in dichloromethane at room temperature for 1 h. The solvent was removed and the residue analyzed by IR and ^1H NMR, which indicated the presence of both 1 and 12. Refluxing in benzene gave no change at short reaction times but led to destruction of the material at longer times. Similar reactions using 6 and 7 also gave no indication of the presence of binuclear species but rather mixtures of mononuclear complex and starting material.

Metal Exchange Reactions. Wilkinson's catalyst (9.3 mg, 10 μmol) and 12 (10.8 mg, 10 μmol) were stirred in 10 mL of benzene at ambient temperature for 2 h. The initially heterogeneous reaction mixture slowly became clear, with a residual yellow-orange color. Removal of the benzene and chromatography gave 7.4 mg of complex 14, identical with authentic material by melting point and IR and ^1H NMR spectra. Similarly, complex 11 gave the rhodium compound 15.

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Registry No. 1, 12120-15-9; 5, 1483-68-7; 6, 75144-31-9; 7, 86374-30-3; 8, 79073-90-8; 9, 87190-02-1; 10, 87190-03-2; 11, 87206-72-2; 12a, 87190-04-3; 14, 87247-40-3; 15, 87247-41-4; chlorotris(triphenylphosphine)rhodium, 14694-95-2; maleic anhydride, 108-31-6; 12b, 87190-05-4.

Reaction of (π-Allyl)palladium Complexes from Allene with Nucleophiles. Synthesis of Conjugated Exocyclic Dienes

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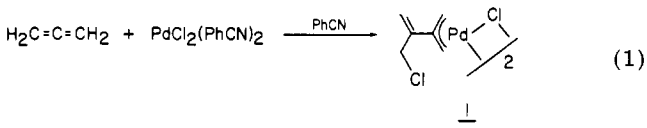
Allene reacts with palladium chloride to produce a (π-allyl)palladium complex (1) containing two allene units connected at their central carbons. This complex reacts with bifunctional nucleophiles such as dimethyl malonate, phenyl cyanomethyl sulfone, *n*-butylamine, and dimethylhydrazine to produce exocyclic dienes 2, 4, 7, and 8 in fair yields, in a process which involves nucleophilic attack at the allylic chloride position followed by attack at a π-allyl terminus. The dianions of acetylacetone, ethyl acetoacetate, and dimethyl succinate were much less efficient in this reaction, giving cyclic material in only low yield.

Introduction

Reaction of allene with dichlorobis(benzonitrile)palladium(II) in benzonitrile produces a high yield of a (π-allyl)palladium complex containing two allene units connected at their central carbons (eq 1).[1-3] Early studies



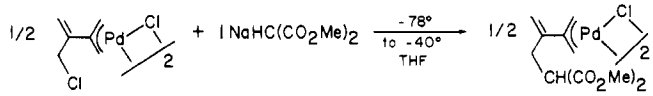
(1)

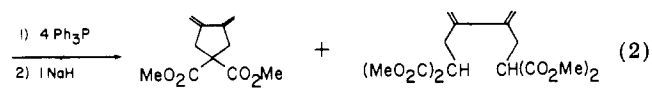
1

with this complex revealed that the bridging chlorides could be exchanged for bromide, iodide, thiocyanate, or acetylacetone and that the complex reacted reversibly with ammonia, pyridine, or *p*-toluidine in a bridge-splitting reaction.[4] In the intervening years, the chemistry of (π-allyl)palladium complexes has been extensively developed, with particular attention to their reactions with nucleophiles.[5-8] Complex 1 is interesting in this regard in that it has two sites available for nucleophilic attack, the allylic chloride and the π-allyl ligand. Herein we report the reactions of complex 1 with bifunctional nucleophiles to produce conjugated exocyclic dienes.

Results and Discussion

Initial studies focussed on the use of dimethyl malonate as the nucleophile. Since (π-allyl)palladium complexes ostensibly do not react with nucleophiles in the absence of added ligands,[8] it was reasoned that reaction of complex 1 with the anion of dimethyl malonate in the absence of added ligands should result in exclusive displacement of the allylic chloride. Subsequent addition of a phosphine ligand (to permit reaction at the π-allyl position) and base (to generate the anion) should permit ring closure generating the desired exocyclic diene 2 (eq 2). Indeed, carrying





(2)

2 3

out this reaction as in eq 2 resulted in a 54% isolated yield of the desired product 2, along with varying amounts of the bis adduct 3. Regardless of reaction conditions bis

(1) R. G. Schultz, *Tetrahedron Lett.*, 301 (1964).
(2) M. S. Lupin and B. L. Shaw, *Tetrahedron Lett.*, 883 (1965).
(3) R. G. Schultz, *Tetrahedron*, **20**, 2809 (1964).
(4) M. S. Lupin, J. Powell, and B. L. Shaw, *J. Chem. Soc. A*, 1687 (1966).
(5) B. M. Trost, *Tetrahedron*, **33**, 2615 (1977).
(6) B. M. Trost, *Accts. Chem. Res.*, **13**, 385 (1980).
(7) B. M. Trost, *Pure Appl. Chem.*, **53**, 2357 (1981).
(8) B. M. Trost and T. J. Fullerton, *J. Am. Chem. Soc.*, **95**, 292 (1973). For a summary of subsequent work in this area see: J. Tsuji, "Organic Synthesis with Palladium Compounds", Springer-Verlag; Berlin, 1980, pp 45–51.

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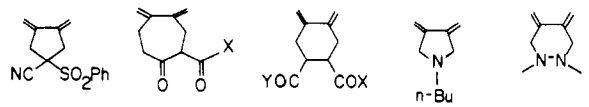
adduct **3** was always the major byproduct and, when excess malonate was used, could be isolated in 78% yield, with only 4% of compound **2** being formed.

In contrast, treatment of complex **1** with the *dianion* of phenyl cyanomethyl sulfone under the conditions in eq 1 resulted in *exclusive* formation of exocyclic diene **4**, with



4 5 6 7 8

no bis adduct detectable in the crude reaction mixture. (Losses during purification resulted in only a 46% isolated yield of this material.) Other dianions were of considerably less use. The dianion of nitromethane decomposed the complex but led to none of the desired diene. The 1,3-dianions of acetylacetone and ethyl acetoacetate produced small amounts of the desired seven-membered ring diene **5** which could not be separated from unidentified byproducts. (The exocyclic diene unit has a characteristic NMR pattern which is easily detected in the presence of other compound.) The 1,2-dianion of dimethyl succinate posed other problems. When LDA (lithium diisopropylamide) was used to generate this dianion, the bis(diisopropylamine) adduct (analogous to **3**) was the major product. Lesser amounts of the desired cyclic diene were obtained. However, this material contained both *O*-methyl and *N*-isopropyl groups, indicating that "ester interchange" with this base used to generate the anion had occurred. When *tert*-butyllithium was used to generate the dianion, the crude product contained substantial amounts of the desired exocyclic diene **6**. However, attempted purification indicated that the cyclic material contained both *O*-methyl and *tert*-butyl groups, indicating that some ester interchange with the base used to form the dianion had occurred. Thus, these two reactions are of little synthetic value.

Treatment of complex **1** with 4 equiv of triphenylphosphine followed by *n*-butylamine produced the five-membered exocyclic diene **7** in 36% isolated yield, although by NMR spectroscopy, the crude material contained no other byproduct. Losses due to complexation of the amine product to the palladium residue accounts for the modest isolated yield. Surprisingly compound **7** showed no tendency to rearrange to the pyrrole but was quite stable after isolation. Finally, 1,2-dimethylhydrazine formed the six-membered diaza exocyclic diene **8** in a modest 29% isolated yield, although again this was primarily due to losses during purification, since the crude reaction mixture contained only **8** and triphenylphosphine.

To gain some insight into these reactions, a number of NMR experiments were performed. Complex **1** has a very characteristic NMR spectrum, with all protons cleanly distinguishable: NMR ($CDCl_3$–Me_4Si) δ 2.86 (s, 2, π-allyl anti H), 4.13 (s, 2, C=C—CH_2Cl), 4.22 (s, 2, π-allyl syn H), 5.47, 5.61 (s, 1 each, =CH_2). Addition of 1 equiv of dimethylamine resulted in the shift of the δ 4.13 peak upfield to δ 3.92 (typical for a C=C—CH_2NR_2 group) with virtually no change in position for any of the other peaks. This indicates that, in the absence of added phosphine, amination occurred exclusively at the *allylic chloride*, converting it to an allylamine. Addition of a second equivalent of dimethylamine resulted in no further change in the spectrum, whereas with the addition of 4 equiv of amine the spectrum degenerated into an uninterpretable mass of peaks.

Treatment of complex **1** with 1 equiv of triphenylphosphine caused the π-allyl proton signals to broaden and shift to δ 3.23 and 3.93 (from the original δ 2.86 and 4.22), indicating that the phosphine had attacked at the palladium and that the π-allyl protons were exchanging in some fashion.[9] The proton signals from the allylic chloride portion of the complex shifted slightly upfield but underwent no significant change, confirming that phosphine had attacked at palladium. Treatment of this monophosphine adduct with 1 equiv of dimethylamine resulted in no change in the NMR spectrum, indicating that this monophosphine complex is *less* reactive than complex **1** to amines.

Treatment of complex **1** with 2 equiv of triphenylphosphine caused more extensive changes in the NMR spectrum. The π-allyl proton signals remained broad and appeared at δ 3.39 and 3.73. The vinyl region became very complex, indicating that the terminal vinyl group was also being affected by phosphine. The methylene absorption remained a sharp singlet but shifted upfield, to δ 4.03. Addition of 1 equiv of *n*-butylamine to the mixture resulted in immediate and quantitative (by NMR) formation of the desired exocyclic diene **7**. The NMR spectrum of this solution was identical with that of pure **7**, except that the CH_2 groups on nitrogen absorbed downfield (δ 2.97 vs. 2.44 and δ 3.90 vs. 3.27) from those of the free amine, indicating that the product in the NMR experiment was complexed to palladium through its nitrogen. (The vinyl proton absorptions were also shifted slightly (δ 0.2) downfield.)

Similarly, treatment of complex **1** with 2 equiv of triphenylphosphine followed by 2 equiv of dimethylamine produced an NMR spectrum consistent with formation of a bis(dimethylamine) adduct similar to **3**, in which the malonate groups were replaced by dimethylamino groups.

Summarizing, these NMR experiments indicate that complex **1** reacts with amines at the allylic chloride position in the absence of added phosphine, does *not* react with amines in the presence of 1 equiv of triphenylphosphine, and rapidly reacts with amines at both the allylic chloride and π-allyl positions in the presence of 2 equiv of triphenylphosphine. This requirement for at *least* 2 equiv of a ligand to permit nucleophilic attack on (π-allyl)palladium complexes is consistent with previous work in this area.[8]

Experimental Section

General Procedures. Melting points were determined with a laboratory device MEL-TEMP capillary melting point apparatus and are uncorrected. Infrared spectra were taken with a Beckman IR 4200 spectrophotometer. The ^1H NMR spectra were recorded on a Nicolet Instrument Corp. NT 360 spectrometer with tetramethylsilane as the internal standard in $CDCl_3$. Chemical shifts and coupling constants are expressed in parts per million and hertz, respectively. NMR experiments were carried out in $CDCl_3$ by using a Varian T-60 instrument. Mass spectra were measured on a V. G. Micromass 16F instrument. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. Preparative chromatography was performed with a Harrison Research Chromatotron 7924 radial layer chromatography apparatus and Merck silica gel 60 PF-254 with $CaSO_4 \cdot {}^1/_2H_2O$ or with Merck Kiesel gel 60 F-254 TLC plates. All reactions were carried out under an argon atmosphere.

Reaction of 1 with Dimethyl Malonate. a. Synthesis of 2. To a THF (1 mL) suspension of complex **1** (0.1 mmol, 51.5 mg) at −78 °C was added a precooled THF (2 mL) solution of $NaCH(CO_2Me)_2$ (0.2 mmol) prepared from dimethyl malonate

(9) (π-Allyl)palladium complexes undergo a number of dynamic processes in the presence of phosphine ligands: K. Vrieze in "Dynamic Nuclear Magnetic Resonance Spectroscopy", L. M. Jackman and F. A. Cotton, Eds., Academic Press, New York, 1975, p 441.

(0.2 mmol, 23 μL) and NaH (50% suspension, 0.25 mmol, 12 mg) stirred at 0 °C for 0.5 h. The mixture was stirred at −78 °C for 1 h and then at −40 °C for 1 h. The mixture was again cooled to −78 °C, and PPh_3 (0.8 mmol, 0.21 g) in 3 mL of THF was added rapidly. This mixture was transferred to a THF (1 mL) suspension of NaH (0.25 mmol, 12 mg) at −78 °C. The temperature was raised to −40 °C and kept for 1 h. The reaction was continued at room temperature for 45 min. The solvent was evaporated under vacuum, and the products were extracted with a 30-mL mixture of hexane and ether (1:1) to give 113 mg of a mixture. Separation by preparative layer chromatography (1:1 hexane/ether) gave 22.5 mg (54%) of pure product as colorless liquid: ^1H NMR (360 MHz, $CDCl_3$, Me_4Si) δ 5.40 (t, 2 H, J = 2.0 Hz, C=CH), 4.96 (s, 2 H, C=CH), 3.73 (s, 6 H, OCH_3), 3.04 (t, 4 H, J = 1.7 Hz, CH_2); IR (neat) 3085 (w), 2953 (m), 1737 (s, =O), 1624 (w), 1432 (m), 1285 (m), 1245 (m), 1200 (m), 885 (m) cm^{-1}; mass spectrum, m/e (relative intensity) 210 (M^+, 7), 179 (7), 178 (14), 151 (20), 150 (58), 119 (24), 91 (100), 59 (17). Anal. Calcd for $C_{11}H_{14}O_4$: C, 62.85; H, 6.71. Found: C, 63.04; H, 6.82. A small amount of **3** was also obtained.

b. Synthesis of 3. To a mixture of the complex **1** (0.50 mmol, 258 mg) and triphenylphosphine (4.0 mmol, 1.05 g) was added 20 mL of THF at room temperature. The resulting homogeneous yellow solution was immediately cooled to −78 °C. Into it was transferred at −78 °C a THF solution (10 mL) of malonate anion prepared from dimethyl malonate (2.2 mmol, 0.25 mL) and sodium hydride (50% suspension, 2.2 mmol, 106 mg) with stirring at 0 °C for 10 min. The mixture was stirred for 2 h and then allowed to warm to room temperature in 2 h. The reaction was continued for 12 h at room temperature.

After the reaction was complete, the heterogeneous yellow mixture was poured into 150 mL of hexane and cooled to 0 °C. Filtration followed by evaporation gave a slightly yellow oil, which was again dissolved in 10 mL of ether. To the solution was added 30 mL of hexane, and the resulting precipitate was filtered. The filtrate was concentrated and chromatographed (1:1 hexane/ether) to give 267 mg of bis adduct **3** (78%) as a white solid: mp 52.5–53.0 °C; ^1H NMR (360 MHz, $CDCl_3$, Me_4Si) δ 5.16 (s, 2 H, C=CH), 5.09 (s, 2 H, C=CH), 3.73 (s, 6 H, OMe), 3.58 (t, 2 H, J = 7.6 Hz, CH), 2.88 (d, 4 H, J = 7.6 Hz, CH_2); IR (neat) 3467 (w), 3092 (m), 1841 (w), 1748 (s, CO), 1698 (w), 1588 (m), 1449 (m), 1434 (m), 1349 (m), 1245 (m), 1195 (m), 914 (m) cm^{-1}; mass spectrum, m/e (relative intensity) 342 (M^+, 6), 311 (24), 282 (52), 247 (43), 219 (46), 191 (58), 159 (58), 151 (64), 131 (55), 91 (85), 59 (100). Anal. Calcd for $C_{16}H_{22}O_8$: C, 56.14; H, 6.48. Found: C, 56.21; H, 6.70.

Reaction of 1 with Phenyl Cyanomethyl Sulfone. Synthesis of 4. To 4 mL of a THF suspension of complex **1** (0.1 mmol, 51.5 mg) was added at −78 °C Na_2PhSO_2CCN in 4 mL of THF formed from $PhSO_2CH_2CN$ (0.2 mmol, 36.2 mg) and *t*-BuLi (1.66 M, 0.4 mmol, 0.24 mL) stirred at −78 °C for 35 min. The yellowish green suspension was stirred at −78 °C for 50 min and then at −40 °C for 40 min. To the mixture was added HMPA (0.2 mmol, 35 μL) followed by addition of triphenylphosphine (0.4 mmol, 105 mg) in 3 mL of THF at −78 °C. The mixture was allowed to warm to room temperature and stirred for 21 h.

After the reaction was complete, precipitates were removed by filtration and the filtrate was concentrated to give a mixture of solid and liquid. The mixture was again dissolved in 40 mL of ether, washed with water (3 × 20 mL) and then brine, dried over Drierite, and concentrated to give 137 mg of a yellow solid, from which 24 mg (46%) of the pure product (white solid, mp 113–113.5 °C) was obtained by preparative layer chromatography (CH_2Cl_2): ^1H NMR (360 MHz, $CDCl_3$, Me_4Si) δ 8.1–7.5 (m, 5 H, ArH), 5.50 (t, 2 H, J = 1.5 Hz, C=CH), 5.04 (s, 2 H, C=CH), 3.31 (dt, 2 H, J = 16.5, 2.6 Hz), 2.89 (d, 2 H, J = 15.9 Hz, CH_2); IR (KBr) 2240 (w, CN), 1451 (m), 1335 (s), 1315 (m), 1162 (s), 1088 (m), 901 (m), 601 (s) cm^{-1}; mass spectrum (relative intensity) 259 (M^+, 1), 167 (2), 143 (100), 118 (47), 117 (91), 116 (67), 91 (26), 77 (55). Anal. Calcd for $C_{14}H_{13}NO_2S$: C, 64.84; H, 5.05; N, 5.40. Found: C, 64.71; H, 5.05; N, 5.57.

Reaction of 1 with the Dianion of Dimethyl Succinate. a. From LDA. To a THF solution of complex **1** (0.50 mmol, 258 mg) and triphenylphosphine (4.0 mmol, 1.05 g) at −78 °C was added the dianion of dimethyl succinate in 10 mL of THF prepared from dimethyl succinate (1.0 mmol, 131 μL) and LDA (2.2 mmol).[10] The mixture was stirred at −78 °C for 1.5 h and then allowed to warm to 25 °C in 1.5 h. The reaction was continued for another 1.5 h at 25 °C.

The resulting mixture was poured into 100 mL of hexane and cooled to 0 °C. Filtration followed by evaporation gave a damp solid, which was dissolved in 2 mL of ether. To this solution was added 10 mL of hexane to precipitate the remaining complexes, which were then removed by filtration. Radial layer chromatography (1:1 hexane/ether) preceded by evaporation gave 69 mg of an acyclic bis adduct of diisopropylamine (25%) and 48 mg of a mixture of cyclic dienes by NMR.

Bis(diisopropylamine) adduct: NMR ($CDCl_3$, Me_4Si) δ 1.02 (d, 24 H, J = 6.4 Hz, $(CH_3)_2CH$), 3.02 (hept, 2 H, J = 6.4 Hz, $(CH_3)_2CHN$), 3.22 (s, 4 H, NCH_2C=C), 5.19 (s, 2 H), 5.30 (s, 2 H, C=CH_2).

Mixture of cyclic dienes: NMR ($CDCl_3$, Me_4Si) δ 0.95 (d, J = 6.2 Hz, $(CH_3)_2CHN$), 2.5–3.3 (m, =CCH_2), 3.66 (s, OCH_3), 4.73 (s), 5.00 (t, J = 2 Hz, =CH_2).

b. From *tert*-Butyllithium. In a 50-mL Airless flask were placed complex **1** (0.50 mmol, 258 mg) and triphenylphosphine (4.0 mmol, 1.05 g) in 20 mL of THF. The mixture was cooled to −78 °C, and the dianion of dimethyl succinate (prepared by slow addition (in 5 min) of a THF solution (5 mL) of dimethyl succinate (1.0 mmol, 131 μL) to *tert*-butyllithium (2.5 M pentane solution, 2.2 mmol, 0.88 mL) in 5 mL of THF at −78 °C followed by stirring for 15 min at the temperature) was added. The mixture was stirred for 1.5 h and allowed to warm to 25 °C in 1.5 h. The reaction was continued for another 2 h at 25 °C. The resulting mixture was poured into 100 mL of hexane and cooled to 0 °C. Evaporation preceded by filtration gave a damp solid mixture, which was dissolved in 2 mL of ether, and 10 mL of hexane was again added to the solution. The yellow precipitates were removed by filtration, and a pale yellow oil was obtained by concentration of the filtrate. Radial layer chromatography (1:1 ether/hexane) gave 93 mg of a mixture of cyclic dienes: NMR ($CDCl_3$–Me_4Si) δ 1.11 (s, $(CH_3)_3C$), 1.17 (s, $(CH_3)_3C$), 2.0, 3.3 (m's, =CCH_2, CHC=O), 3.53 (s, OCH_3), 4.67, 4.99 (t's, C=CH_2).

Reaction of 1 with *n*-Butylamine. Synthesis of 7. In a 50-mL round-bottom flask were placed complex **1** (0.50 mmol, 258 mg) and triphenylphosphine (4.4 mmol, 1.16 g), and the system was degassed with argon. To the mixture was added 30 mL of dry THF to give yellow homogeneous solution. After the mixture was cooled to 0 °C, triethylamine (4.0 mmol, 0.56 mL) was added. Addition of butylamine (1.0 mmol, 0.1 mL) caused the formation of a yellow precipitate. Then NaH (50% suspension, 1 mmol, 48 mg) was added. After the solution was stirred at 25 °C for 0.5 h, another 1 mmol of NaH was added. The reaction was continued for 2 h at reflux temperature under argon. The resulting mixture was poured into 100 mL of hexane and cooled to 0 °C. Precipitates were removed by filtration, and the filtrate was concentrated. To the mixture was added 20 mL of hexane and 1 mL of triethylamine with stirring at 0 °C. Filtration followed by evaporation gave 0.45 g of a pale yellow viscous liquid, which consisted of the desired diene, triphenylphosphine, and oil from NaH suspension. The mixture was then subjected to radial layer chromatography (1:1 hexane/ether) to give 55 mg of the pure product (36% yield): ^1H NMR (360 MHz, $CDCl_3$, Me_4Si) δ 5.37 (t, 2 H, J = 1.8 Hz, =CH_2), 4.92 (s, 2 H, =CH_2), 3.29 (t, 4 H, J = 1.6 Hz, =CCH_2N), 2.46 (t, 2 H, J = 7.6 Hz, NCH_2), 1.6–0.9 (m, 7 H, $CH_3CH_2CH_2$); IR (neat) 3080 (w), 1634 (w), 1464 (m), 1377 (m), 1150 (m), 877 (s) cm^{-1}; mass spectrum, m/e (relative intensity) 151 (M^+, 39), 150 (7), 136 (7), 109 (50), 108 (100), 94 (34). Anal. Calcd for $C_{10}H_{17}N$: C, 79.41; H, 11.33; N, 9.26. Found: C, 79.18; H, 11.11; N, 9.05.

Reaction of 1 with Dimethylhydrazine. Synthesis of 8. To a mixture of **1** (0.5 mmol, 258 mg), triphenylphosphine (4 mmol, 1.05 g), and molecular sieves 3A (2 g) in 30 mL of THF was added a THF (3 mL) solution of *N,N'*-dimethylhydrazine (1.0 mmol) (generated in situ from *N,N'*-dimethylhydrazine dihydrochloride (1.0 mmol, 133 mg) and 2 equiv of *n*-BuLi (2.2 M in hexane, 2.0 mmol, 0.9 mL) at 0 °C). The yellow suspension was stirred at 25 °C overnight.

After the reaction was complete, 100 mL of pentane was added to the resulting mixture. The yellow solid was removed by fil-

(10) N. R. Long and M. W. Rathke, *Synth. Commun.*, 11, 687 (1981).

tration, and the filtrate was washed with water and then dried. The mixture was concentrated and subjected to Kugelrohr distillation (80–90 °C (0.75 mmHg)) to give 40 mg of a colorless liquid (29%): ^{1}H NMR (360 MHz, $CDCl_3$, Me_4Si) δ 5.22 (d, 2 H, J = 0.8 Hz, $=CH_2$), 4.79 (d, 2 H, J = 1.2 Hz, $=CH_2$), 3.41 (br, 4 H, $=CCH_2N$), 2.45 (s, 6 H, CH_3N); IR (neat) 3078 (m), 1635 (m), 1450 (m), 1239 (m), 1103 (m), 887 (s), 753 (m) cm^{-1}. mass spectrum, m/e (relative intensity) 138 (M^+, 94), 123 (100), 108 (17). Anal. Calcd for $C_8H_{14}N_2$: C, 69.52; H, 10.21; N, 20.27. Found: C, 69.48; H, 10.06; N, 20.37.

Acknowledgment. This research was supported by Grant #CHE 8200522 from the National Science Foundation. High field NMR spectra were obtained on instruments in the Colorado State University Regional NMR Center, funded by National Science Foundation Grant #CHE 7818581.

Registry No. **1**, 12090-04-9; **2**, 87185-05-5; **3**, 87185-06-6; **4**, 87185-07-7; **7**, 87185-08-8; **8**, 87185-09-9; $NaCH(CO_2Me)_2$, 18424-76-5; PPh_3, 603-35-0; Na_2PhSO_2CCN, 87185-10-2; dimethyl malonate, 108-59-8; phenyl cyanomethyl sulfone, 7605-28-9; dimethyl succinate, 106-65-0; dimethyl succinate (dianion), 87185-11-3; 1,4-bis(diisopropylamino)-2,3-dimethylenebutane, 87185-12-4; *n*-butylamine, 109-73-9; dimethylhydrazine, 30260-66-3.

Luminescence of Organometallic Lanthanide Compounds. Tetrahydrofuran Adducts of Tricyclopentadienylterbium(III) and Tris(methylcyclopentadienyl)terbium(III)

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The photoluminescence of the title compounds has been studied at room and cyrogenic temperatures. Transitions from the luminescent $^5D_4$ level to every member of the ground ^7F_J manifold (J = 0–6) were observed. When examined at 2-Å resolution, each J–J transition was found to contain a very large number of components and the resolution of these improved noticeably at 77 K. Group theoretical analysis of the various J levels was carried out for C_{3v} symmetry, and the results used to predict the number of allowed transitions permissible for each transition. Almost without exception fewer peaks were observed than were predicted, and this observation prevented a complete theoretical analysis of the data. However, in the $^5D_4 \rightarrow {}^7F_0$ transition of $Tb(Cp)_3(THF)$ a full determination of the origin of all bands could be made, and it was established that emission took place out of all crystal field components of the $^5D_4$ excited state. At room temperature, the cyclopentadienyl compound appeared to be spectroscopically identical with the methylcyclopentadienyl compound, but at cryogenic temperatures significant differences exist between the two.

Introduction

Investigation of the organometallic chemistry of lanthanide ions has become an area of intense research activity, with the complexes containing cyclopentadienyl (Cp) ligands being the best understood.[1-5] Much research has centered on identifying the differences between organolanthanide and organotransition-metal complexes in order to exploit the special features of lanthanides to provide materials with new types of physical, chemical, and catalytic properties. One main area of difference is the role of covalency in the metal–ligand bonding. It is generally agreed that the bonding in lanthanide organometallic compounds is essentially totally ionic in nature.[5,6]

To characterize organometallic lanthanide complexes, most workers have employed techniques suited for structural determination, such as X-ray crystallography and NMR spectroscopy. The use of optical spectroscopy as a means of characterization has not been extensively exploited, and only a few studies are in the literature. The f–f absorption bands of $Yb(Cp)_3$, $Er(Cp)_3$, and several Lewis base adducts of these have been studied down to liquid-helium temperatures,[7-9] and it became established that little perturbation of the free ion energy levels resulted after complexation. However, the appearance of a new charge-transfer band was noted in the organometallic compounds,[7-9] and the existence of such transitions was deduced in other studies involving different compounds.[10]

Even less work has been carried out by using luminescence methods, in spite of the situation where it is known that the emission spectra associated with f–f transitions generally consists of only a few well-separated band systems. It has been determined that $Gd(Cp)_3$ and $La(Cp)_3$ exhibit strong emission at both room and cryogenic temperatures,[8] although this luminescence is certainly localized on the Cp ligands. The f–f luminescence bands of $Yb(Cp)_3$ and several adducts of this compound have also been re-

(1) "Organometallics of the f-Elements"; Marks, T. J., Fisher, R. D., Eds.; D. Reidel Publishing Co.: Dordrecht, Holland, 1979.
(2) Marks, T. J. *Prog. Inorg. Chem.* **1978**, *24*, 51.
(3) Marks, T. J.; Ernst, R. D. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., et al., Eds.; Pergamon Press: Oxford, 1982; Vol. 3, Chapter 21.
(4) Evans, W. J. In "The Chemistry of the Metal Carbon Bond"; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1982; Chapter 12.
(5) Raymond, K. N.; Eigenbrot, C. W. *Acc. Chem. Res.* **1980**, *13*, 276.
(6) Moeller, T. In "Comprehensive Inorganic Chemistry"; Trotman-Dickenson, A. F., et. al., Eds.; Pergamon Press: Oxford, 1973; Chapter 44.
(7) Pappalardo, R.; Jorgensen, C. K. *J. Chem. Phys.* **1967**, *46*, 632
(8) Pappalardo, R. *J. Chem. Phys.* **1968**, *48*, 1545.
(9) Schlesener, C. J.; Ellis, A. B. *Organometallics* **1983**, *2*, 529.
(10) Tsutsui, M.; Ely, N. M. *J. Am. Chem. Soc.* **1975**, *97*, 1280.
(11) Pappalardo, R.; Losi, S. *J. Inorg. Nucl. Chem.* **1965**, *27*, 733.

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