Cyclooctatetraene Complexes of Niobium and Tantalum and the Structure of Nb(η^4-C$_8$H$_8$)[η^5-C$_8$H$_8$(C$_6$H$_5$)][(CH$_3$)$_2$AsC$_6$H$_4$As(CH$_3$)$_2$]

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Abstract: Cyclooctatetraene complexes of the type M(C$_8$H$_8$)$_2$R (M = Nb, Ta; R = C$_6$H$_5$, CH$_3$) and Ta(C$_8$H$_8$)(CH$_3$)$_3$ have been prepared employing [K$^+$]$_2$[C$_8$H$_8$]$^{2-}$ as the reducing agent and source of C$_8$H$_8$. In the former the η^4 and η^8 rings interconvert on the NMR time scale with $\Delta G^\ddagger_{337}$ = 15.7–17.5 kcal mol^{-1} depending on M and R. Except where R = C$_6$H$_5$ both form adducts with some donor ligands such as (CH$_3$)$_2$PCH$_2$CH$_2$P(CH$_3$)$_2$. When R = C$_6$H$_5$, forcing conditions give complexes containing the 2,3,4,5,6-η-*endo*-8-phenylbicyclo[5.1.0]octadienyl ligand, e.g., Nb(η^4-C$_8$H$_8$)[η^5-C$_8$H$_8$(C$_6$H$_5$)]-[(CH$_3$)$_2$AsC$_6$H$_4$As(CH$_3$)$_2$], the structure of which was determined by x-ray methods. The cyclopropyl ring is exo to the metal and the phenyl substituent endo, the first instance where the geometry of this bicyclic ligand has been established. The η^4-C$_8$H$_8$ and diars geometries are normal. Similar complexes are obtained when electrophiles (E = H$^+$, D$^+$, and C(C$_6$H$_5$)$_3$$^+$) attack [M($\eta^4$-C$_8H_8$)($\eta^3$-C$_8H_8$)$_2$]$^-$ in the presence of (CH$_3$)$_2$PCH$_2$CH$_2$P(CH$_3$)$_2$. The facility of the η^8-C$_8$H$_8$ → (e.g.) η^4-C$_8$H$_8$ process suggests that complexes containing η^8-C$_8$H$_8$ are potentially valuable catalysts (or catalyst precursors) for reactions taking place at the metal center.

Cyclooctatetraene complexes are known for most transition metals[1] as well as for several lanthanides and actinides.[2] Cyclooctatetraene is a versatile ligand which adapts to the metal's requirements by increasing or decreasing the number of formal olefin–metal bonds, extremes being planar η^8 bonding, which predominates for group 4 and 5 metals, lanthanides, and actinides, and η^2 bonding, which is rare and known only for late metals like Cu.[3] The predominant mode is η^4 or η^6 in which only the bonded carbons lie in a plane.[4]

Planar η^8-C$_8$H$_8$ may be viewed either as a dianion or as a neutral tetraene. Each is reasonable, the first because one would otherwise have to postulate unusually low formal metal oxidation states like Ti(0) in Ti(η^4-C$_8$H$_8$)(η^8-C$_8$H$_8$),[5] the second because, formally at least, η^8-C$_8$H$_8$ can become η^6-C$_8$H$_8$ or η^4-C$_8$H$_8$, or be displaced entirely. Overall, η^8-C$_8$H$_8$ could be called a "protecting" ligand, since each of the steps, $\eta^8 \rightarrow \eta^6 \rightarrow \eta^4$, creates a coordination site at a potentially reactive metal in a low formal oxidation state, or, alternatively, simply as a "stabilizing" ligand analogous to η^5-C$_5$H$_5$.[6]

Several C$_8$H$_8$ complexes of niobium and tantalum have been prepared in order to determine the predominant C$_8$H$_8$ bonding modes and to study the relationship of bonding to reactivity with simple donor ligands, reactions which may be models for more general reactions at the metal center. A crystal structure of one product shows that cyclooctatetraene can play a more active role by accepting a ligand transferred from the metal.

Experimental Section

Preparations. All manipulations were done in a nitrogen-filled Vacuum Atmospheres drybox. Solutions of [K$^+$]$_2$[C$_8$H$_8$]$^{2-}$ were prepared by stirring the appropriate quantities of C$_8$H$_8$ (redistilled under nitrogen) and potassium pieces in THF overnight. Niobium and tantalum pentahalides were used as received. Solvents were passed through 4A molecular sieve columns and degassed before use.

Compounds were analyzed at the Central Research and Development Department. The most air and moisture sensitive consistently analyzed low in carbon (up to ca. 1%), even though drybox procedures were employed and all reasonable precautions were taken to ensure sample purity. Less sensitive derivatives usually analyzed satisfactorily.

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1. Preparation of Nb(C$_8$H$_8$)$_2$(C$_6$H$_5$). NbCl$_5$ (50 g) in 600 ml of toluene at −78 °C was treated with 800 ml of 0.46 M [K$^+$]$_2$[C$_8$H$_8$]$^{2-}$ in THF with stirring over a period of 2 hr. After an additional 1 hr, 98 ml of 17.82% LiC$_6$H$_5$ in diethyl ether-benzene (23:77) was added over 1 hr and the final mixture was warmed to room temperature. Potassium chloride was separated by centrifugation in gas-tight polypropylene bottles, homogenized with 800 ml of THF, and again separated by centrifugation. The decanted solutions were combined and filtered and the solvent was removed in vacuo to a volume of ~600 ml. Solids were filtered off and the volume further reduced to ~100 ml. Solids from a second filtration combined with the first were dried in vacuo; yield 74 g. The crude product was stirred in 500 ml of acetonitrile, filtered off, washed with 200 ml of diethyl ether, and stirred into 500 ml of dichloromethane. Filtering and reducing the filtrate volume to ~100 ml gave 27 g of Nb(C$_8$H$_8$)$_2$(C$_6$H$_5$) which could be recrystallized from THF (35 g in 600 ml at 60 °C) or CH$_2$Cl$_2$ as red-brown plates. The acetonitrile wash above contained 18 g of [Li(CH$_3$CH)$_x$]$^+$[Nb(C$_8$H$_8$)$_3$]$^-$ which could be recrystallized from THF as the [Li(THF)$_4$]$^+$ salt.

Anal. Calcd for NbC$_{22}$H$_{21}$: C, 69.85; H, 5.60; Nb, 24.56. Found: C, 68.87; H, 5.60; Nb, 24.44. ^{1}H NMR (τ, CD$_2$Cl$_2$, 0 °C): 2.56 (2, dd, J = 7.5 and 1.5 Hz, ortho), 3.09 (3, m, meta and para), 4.10 (8, s, C$_8$H$_8$), 4.57 (8, s, C$_8$H$_8$).

2. Preparation of Nb(C$_8$H$_8$)$_2$(CH$_3$). Nb(CH$_3$)$_2$Cl$_3$ (8.52 g, 37.2 mmol) and NbCl$_5$ (9.5 g, 35.2 mmol) were stirred in toluene at room temperature for 3 hr. After cooling to −78 °C, a solution of [K$^+$]$_2$[C$_8$H$_8$]$^{2-}$ (0.47 M in THF, 300 ml, 140 mmol) was added over 45 min and the mixture was warmed to room temperature and stood overnight. The mixture was centrifuged to remove KCl and the volume was reduced to near dryness, filtering periodically to give 8.6 g of crude Nb(C$_8$H$_8$)$_2$(CH$_3$). The product was recrystallized from hot THF by cooling to −30 °C overnight.

Anal. Calcd for NbC$_{17}$H$_{19}$: C, 64.57; H, 6.05. Found: C, 63.25; H, 6.00. ^{1}H NMR (τ, CD$_2$Cl$_2$, 0 °C): 4.14 (8, s, C$_8$H$_8$), 4.65 (8, s, C$_8$H$_8$), 9.83 (3, s, CH$_3$).

3. Preparation of Ta(C$_8$H$_8$)$_2$(C$_6$H$_5$). TaCl$_5$ (10.0 g) in 600 ml of toluene was stirred for ca. 15 min until all of it nearly dissolved. Zn(C$_6$H$_5$)$_2$ (6.08 g) was added as a solid and gelatinous ZnCl$_2$ filtered from the yellow solution. TaCl$_5$ (10.0 g) was added and the mixture was stirred for ca. 15 min then cooled to −78 °C. A 0.47 M solution of [K$^+$]$_2$[C$_8$H$_8$]$^{2-}$ in tetrahydrofuran (240 ml) was added dropwise over 1 hr. The mixture was warmed to room temperature and centrifuged to remove KCl (filtrate A). The KCl was homogenized in 750 ml of THF and again removed by centrifugation (filtrate B). The volume of filtrate B was reduced in vacuo and a total of 6.0 g of Ta(C$_8$H$_8$)$_2$(C$_6$H$_5$) filtered off periodically (filtrate C). Filtrate A gave 7.5 g of brown solid (by a similar isolation procedure) which was extracted with 250 ml of dichlorometh-

Table I. $\Delta G^{\ddagger}$ Values for the η^8-$C_8H_8 \rightleftharpoons \eta^4$-$C_8H_8$ Process

	$\Delta G^{\ddagger}_{337}$, kcal mol^{-1}
Nb(η^8-C_8H_8)(η^4-C_8H_8)(CH$_3$)	17.5 ± 0.5^a
Nb(η^8-C_8H_8)(η^4-C_8H_8)(C_6H_5)	≥17^b
Ta(η^8-C_8H_8)(η^4-C_8H_8)(CH$_3$)	15.7 ± 0.2
Ta(η^8-C_8H_8)(η^4-C_8H_8)(C_6H_5)	16.5 ± 0.2
Ti(η^8-C_8H_8)(η^4-C_8H_8)	16.7 ± 0.2

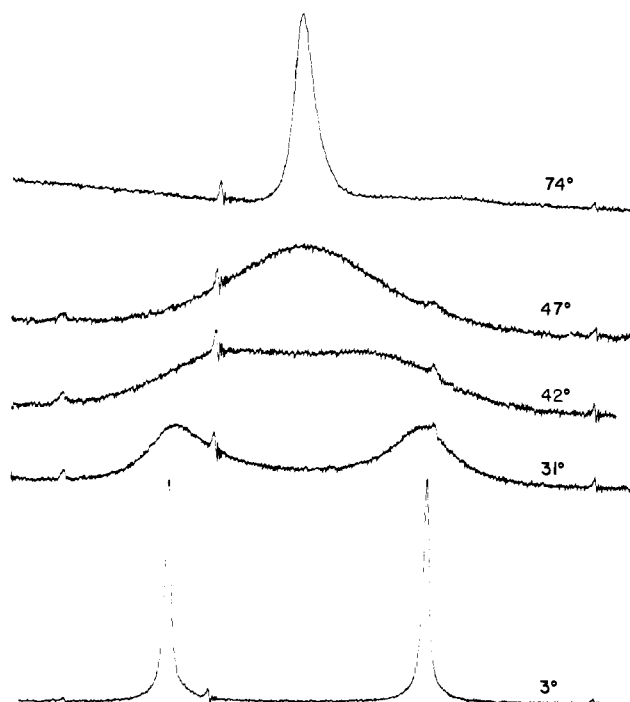^{a} Accuracy limited by peak broadening. ^{b} Accuracy limited by peak broadening and decomposition.

Figure 1. The variable temperature 100-MHz ^{1}H NMR spectrum of the C_8H_8 ligands in Ta(η^8-C_8H_8)(η^4-C_8H_8)(CH$_3$) in o-dichlorobenzene.

ane. The extract was filtered and the filtrate combined with C, reduced to ~50 ml in vacuo, and stood at −30 °C overnight to give 3.5 g of Ta(C_8H_8)$_2$(C_6H_5); total yield 9.5 g (37%).

Anal. Calcd for TaC$_{22}$H$_{21}$: C, 56.65; H, 4.55. Found: C, 56.31; H, 4.61. ^{1}H NMR (τ, CD$_2$Cl$_2$, 0 °C): 2.45 (2, dd, J = 1.5 and 7.5 Hz, ortho), 3.05 (3, m, meta and para), 4.08 (8, s, C_8H_8), 4.61 (8, s, C_8H_8).

4. Preparation of Ta(C_8H_8)$_2$(CH$_3$). Ta(CH$_3$)$_3$Cl$_2$ (5.0 g) and TaCl$_5$ (12.1 g) were stirred in toluene overnight. The solution of Ta(CH$_3$)Cl$_4$ was cooled to −78 °C and 213 ml of 0.47 M [K$^+$]$_2$[C_8H_8]$^{2-}$ was added over 1 hr. The mixture was warmed to room temperature, centrifuged to remove KCl, reduced in volume to ca. 150 ml, and filtered to give 8.0 g of red-brown Ta(C_8H_8)$_2$(CH$_3$). A 7.5-g sample was recrystallized from 150 ml of dichloromethane by volume reduction to give 5.0 g of Ta(C_8H_8)$_2$(CH$_3$) as glittering red-brown, almost black, plates.

Anal. Calcd for TaC$_{17}$H$_{19}$: C, 50.38; H, 4.73. Found: C, 49.68; H, 4.72. ^{1}H NMR (τ, CD$_2$Cl$_2$, 0 °C): 4.09 (8, s, C_8H_8), 4.64 (8, s, C_8H_8), 9.95 (3, s, CH$_3$); see Figure 1 for variable temperature spectra.

5. Preparation of Ta(C_8H_8)(CH$_3$)$_3$. Ta(CH$_3$)$_3$Cl$_2$ (40 g) in toluene (1 l.) was cooled to −78 °C and 300 ml of 0.47 M [K$^+$]$_2$[C_8H_8]$^{2-}$ was added over 2 hr. The solution was warmed to room temperature and stood for 2 hr. KCl was removed by centrifugation and the volume was reduced to ca. 25 ml, filtering periodically, to give 35.4 g of crude Ta(C_8H_8)(CH$_3$)$_3$. The product may be purified by recrystallization in high yield from hot toluene by cooling to −30 °C; Ta(C_8H_8)$_2$(CH$_3$) is the impurity. It also sublimes without decomposition (100 °C, 1 μ).

Anal. Calcd for TaC$_{11}$H$_{17}$: C, 40.01; H, 5.19; Ta, 54.80. Found:

C, 39.83; H, 5.23; Ta, 54.80. ^{1}H NMR (τ, C_6D_6): 4.03 (8, s, C_8H_8), 9.17 (9, s, CH$_3$). Mass spectrum: 330.0810 (calcd 330.0787). Cryoscopic molecular weight in benzene: 351 (calcd 330).

6. Preparation of Ta(C_8H_8)(CH$_3$)$_3$(dmpe) (dmpe = (CH$_3$)$_2$-PCH$_2$CH$_2$P(CH$_3$)$_2$). Ta(C_8H_8)(CH$_3$)$_3$ (2.0 g) in toluene (40 ml) was treated with 0.95 g of dmpe. Crystals formed immediately. After 4 hr at −40 °C the product was filtered off, washed with pentane, and vacuum dried; yield 2.5 g (85%) of green-black crystals.

Anal. Calcd for TaC$_{17}$H$_{33}$P$_2$: C, 42.51; H, 6.92; P, 12.90. Found: C, 42.53; H, 6.99; P, 13.31. ^{1}H NMR (τ, C_6D_6): 4.27 (8, t, J = 1.1 Hz, C_8H_8), 7.5-8.4 (4, m, dmpe CH$_2$'s), 8.73 (6, d, J = 8 Hz, dmpe CH$_3$ set), 8.87 (6, d, J = 8 Hz, dmpe CH$_3$ set), 9.61 (3, dd, J = 3 and 13 Hz, single CH$_3$), 11.05 (6, dd, J = 9.5 and 11.5 Hz, CH$_3$ pair). At 220 MHz the dmpe CH$_3$ sets are well separated. ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$): 7.81 and 18.97 ppm downfield from 85% H$_3$PO$_4$ (doublets, J = 11 Hz).

7. Preparation of Ta(C_8H_8)(CH$_3$)$_3$(diars) (diars = (CH$_3$)$_2$As-C_6H_4As(CH$_3$)$_2$). Hexane (30 ml) was added to a solution of 1.0 g of Ta(C_8H_8)(CH$_3$)$_3$ and 0.87 g of diars in 20 ml of toluene and the solution stood at −30 °C overnight to give deep olive-green plates which were filtered off, washed with pentane, and dried; yield 0.80 g.

Anal. Calcd for TaC$_{21}$H$_{33}$As$_2$: C, 40.93; H, 5.49; As, 24.32. Found: C, 40.70; H, 5.40; As, 23.70. ^{1}H NMR (τ, CD$_2$Cl$_2$, −20 °C, phenyl protons omitted): 4.22 (8, s, C_8H_8), 8.66 and 8.79 (each 6, s, diars CH$_3$ set), 9.52 (3, s, CH$_3$), 11.05 (6, s, CH$_3$ set).

8. Preparation of Ta(C_8H_8)(CH$_3$)$_3$[P(CH$_3$)$_3$]. Ta(C_8H_8)(CH$_3$)$_3$ (330 mg) in 5 ml of toluene was treated with 0.5 ml of PMe$_3$. Pentane (5 ml) was added, the sample stood for 1 hr at −30 °C, and 270 mg of red-brown crystals was filtered off.

Anal. Calcd for TaC$_{14}$H$_{26}$P: C, 41.39; H, 6.44. Found: C, 40.56; H, 6.29. ^{1}H NMR (τ, CD$_2$Cl$_2$, −70 °C): 4.66 (8, d, J = 1.4 Hz, C_8H_8), 8.79 (9, d, $J \approx$ 7 Hz, P(CH$_3$)$_3$), ca. 8.9 (3, d (partly obscured at 100 MHz), CH$_3$), 10.02 (6, d, J = 13 Hz, CH$_3$ set).

9. Preparation of Ta(C_8H_8)$_2$(CH$_3$)[P(CH$_3$)$_3$]. PMe$_3$ (50 μl) was added to 0.25 g of Ta(C_8H_8)$_2$CH$_3$ in ca. 5 ml of CH$_2$Cl$_2$. Removal of all volatiles in vacuo left dark olive-green T(C_8H_8)$_2$-(CH$_3$)[P(CH$_3$)$_3$] which was characterized by ^{1}H NMR only.

^{1}H NMR (τ, CD$_2$Cl$_2$, −30 °C): 5.04 (16, d, J = 5 Hz, C_8H_8), 8.70 (9, d, J = 8 Hz, P(CH$_3$)$_3$), 10.09 (3, d, J = 11 Hz, CH$_3$).

10. Observation of M(C_8H_8)$_2$(CH$_3$)(dmpe) (M = Nb, Ta). These adducts can be observed at −30 °C by ^{1}H NMR but not isolated at room temperature.

^{1}H NMR (τ, CD$_2$Cl$_2$, −30 °C): for M = Ta, 4.37 (16, poor dd, $J \approx$ 1.8 and 2.0 Hz, C_8H_8), 7.73 (4, AB quartet, dmpe CH$_2$'s), 8.52 (6, d, $J \approx$ 7 Hz, dmpe CH$_3$ set), 8.87 (6, d, $J \approx$ 8, dmpe CH$_3$ set), 14.07 (3, dd, J = 8 and 12 Hz, CH$_3$); for M = Nb, 4.43 (16, poor dd, $J \approx$ 1.8 and 2.0 Hz, C_8H_8), 7.80 (4, AB quartet, dmpe CH$_2$'s), 8.51 (6, d, $J \approx$ 7 Hz, dmpe CH$_3$ set), 8.91 (6, d, $J \approx$ 8 Hz, dmpe CH$_3$ set), 14.24 (3, dd, J = 6 and 12 Hz, CH$_3$).

11. Preparation of Nb(C_8H_8)[C_8H_8(C_6H_5)](dmpe). Nb(C_8H_8)$_2$(C_6H_5) (3.0 g) and 1.4 g of dmpe were dissolved in 100 ml of toluene and the solution was heated to reflux for 5 hr. The solution was cooled to room temperature and filtered leaving fluffy brown crystals. This product was dissolved in 100 ml of boiling toluene and the solution was filtered leaving some dark brown solid behind. Cooling gave 1.5 g of Nb(C_8H_8)[C_8H_8(C_6H_5)](dmpe) which was recrystallized from THF with diethyl ether.

Anal. Calcd for C$_{28}$H$_{37}$P$_2$Nb: C, 63.64; H, 7.06; P, 11.72; Nb, 17.58. Found: C, 63.57; H, 7.21; P, 11.16; Nb, 16.98. See Figure 2 for the 220-MHz ^{1}H NMR spectrum and Table II.

12. Preparation of Nb(C_8H_8)[C_8H_8(C_6H_5)](diars). Nb(C_8H_8)$_2$(C_6H_5) (2.0 g) and 1.7 g of diars were placed in 50 ml of THF and the solution was refluxed for 3 hr, cooled to room temperature, filtered, reduced to a volume of ca. 20 ml, and let stand at −30 °C overnight to give 1.65 g of red crystals. Nb(C_8H_8)[C_8H_8(C_6H_5)](diars) may be recrystallized from THF with hexane. This sample retained ca. 1 mol of THF according to ^{1}H NMR.

Anal. Calcd for C$_{36}$H$_{45}$OAs$_2$Nb: C, 58.87; H, 5.90; As, 20.40; Nb, 12.65. Found: C, 59.00; H, 6.10; As, 19.71; Nb, 13.08. See Table II for ^{1}H NMR data.

13. Preparation of Ta(C_8H_8)[C_8H_8(C_6H_5)](dmpe). Ta(C_8H_8)$_2$(C_6H_5) (2.0 g) and dmpe (0.75 g) were heated in re-

Figure 2. The 220-MHz ^{1}H NMR spectrum of Nb(η^4-C$_8$H$_8$)[η^5-C$_8$H$_8$(C$_6$H$_5$)](dmpe) in THF-d_8 (η^4-C$_8$H$_8$ scale is 500 Hz; remainder is on the 2500-Hz scale). (*) THF-d_x ($x < 8$). The upfield peak partially hides one dmpe methyl doublet.

Table II. Tabulation of ^{1}H Data for "M(C$_8$H$_8$)$_2$(C$_6$H$_5$)(L-L)" Complexes^a

	Ta(dmpe)^b	Ta(diars)	Nb(dmpe)	Nb(diars)
Static C$_8$H$_8$^{c}	4.70 (t)	4.53 (t)	4.66 (t)	4.50 (t)
	5.81 (q)	5.58 (t)	5.73 (q)	5.55 (dd)
	6.95 (m)	6.75 (dd)	6.86 (m)	6.60 (dd)
		8.75 (t)	8.94 (m)	8.86 (m)
	9.25 (m)	9.52 (m)	9.31 (m)	9.58 (m)
	10.89 (dd)	10.68 (t)	10.95 (t)^d	10.89 (poor t)
L-L^e	7.99 (d)	7.96 (s)	7.94 (d)	7.97 (s)
	8.27 (d)	8.06 (s)	8.31 (d)	8.09 (s)
	8.67 (d)	8.50 (s)	8.65 (d)	8.52 (s)
	8.79 (d)	8.66 (s)	8.83 (d)	8.64 (s)
Dynamic C$_8$H$_8$^{f}	4.90 (t)	4.85 (s)	4.93 (t)	4.89 (s)

^{a} τ in CD$_2$Cl$_2$ at 220 MHz unless otherwise stated (phenyl resonances omitted). Note sample in Figure 2 run in THF-d_8. ^{b} At 100 MHz. ^{c} All H–H couplings are 7–10 Hz. ^{d} In THF-d_8 (see Figure 2). ^{e} J_{CH_3P} = 6–8 Hz. ^{f} J_{H_8PP} = 1.5–2.0 Hz.

fluxing THF for 18 h. Cooling to −30 °C for several hours gave 1.7 g of Ta(C$_8$H$_8$)[C$_8$H$_8$(C$_6$H$_5$)](dmpe) containing ca. 1 mol of THF of crystallization. Recrystallization from CH$_2$Cl$_2$ gave orange crystals containing ca. 1 mol of CH$_2$Cl$_2$.

Anal. Calcd for TaC$_{29}$H$_{39}$P$_2$Cl$_2$: C, 49.65; H, 5.62; Cl, 10.11. Found: C, 50.71; H, 5.75; Cl, 9.48. See Table II for ^{1}H NMR data.

14. Preparation of Ta(C$_8$H$_8$)[C$_8$H$_8$(C$_6$H$_5$)](diars). The preparation is the same as the preparation of Nb(C$_8$H$_8$)-[C$_8$H$_8$(C$_6$H$_5$)](diars) from 1.5 g of Ta(C$_8$H$_8$)$_2$(C$_6$H$_5$) and 0.92 g of diars except the solution was refluxed for 8 h; yield 1.0 g. Shorter reaction times gave mixtures of product and starting material.

Anal. Calcd for TaC$_{32}$H$_{37}$As$_2$: C, 51.08; H, 4.95; As, 19.91. Found: C, 50.85; H, 4.90; As, 19.15.

The ^{1}H NMR spectrum is similar to that shown in Figure 2. See Table II for chemical shifts.

15. Preparation of Nb(C$_8$H$_8$)(C$_8$H$_9$)(dmpe). [Li(THF)$_4$]$^+$-[Nb(C$_8$H$_8$)$_3$]$^-$ (10.0 g) and dmpe (2.6 g) in 100 ml of THF (well-stirred and cooled to −78°C) were treated dropwise over $\frac{1}{2}$ h with a solution of 1.3 ml of CF$_3$CO$_2$H in 50 ml of THF. The mixture was warmed to room temperature and stripped to an orange syrup which was extracted with ca. 250 ml of toluene with stirring for 3 h. The mixture was filtered and the filtrate stripped to a syrup in which red-orange granular crystals formed slowly. After several hours the product was filtered, washed briefly with toluene, then diethyl ether, and dried in vacuo; yield 0.70 g (11%). A small sample was recrystallized from THF for analysis.

Anal. Calcd for NbC$_{22}$H$_{33}$P$_2$: C, 58.41; H, 7.35. Found: C, 58.46; H, 7.38.

The ^{1}H NMR spectrum is similar to that in Figure 3 with minor variations.

16. Preparation of Nb(C$_8$H$_8$)(C$_8$H$_8$D)(dmpe). The procedure was

Figure 3. The 220-MHz ^{1}H NMR spectrum of Ta(η^4-C$_8$H$_8$)(η^5-C$_8$H$_9$)(dmpe) in THF-d_8 (η^4-C$_8$H$_8$ scale is 500 Hz; remainder is on the 2500-Hz scale). (*) THF-d_x ($x < 8$).

identical with that for Nb(C$_8$H$_8$)(C$_8$H$_9$)(dmpe) employing CF$_3$CO$_2$D; yield 1.20 g (19%).

The stripped solvent was saved and analyzed for C$_8$ hydrocarbons by GC/mass spectrometry.

Hydrocarbon	Total vs. Nb
C$_8$H$_8$ (>97%) C$_8$H$_7$D (<3%)	27% (4.6 mmol)
C$_8$H$_{10}$ (5−10%) C$_8$H$_9$D (85−90%) C$_8$H$_8$D$_2$ (2−7%)	5% (0.8 mmol, isomer A)
C$_8$H$_{10}$ (2−7%) C$_8$H$_9$D (83−88%) C$_8$H$_8$D$_2$ (8−12%)	7−8% (1.4 mmol, isomer B)

The ^{1}H NMR spectrum is essentially identical with that of Nb(C$_8$H$_8$)(C$_8$H$_9$)(dmpe) except there is some loss of H–H coupling in the C$_8$H$_9$ peak(s) between τ 7.5 and 8.0.

17. Preparation of Ta(C$_8$H$_8$)(C$_8$H$_9$)(dmpe). The procedure was identical with that for Nb(C$_8$H$_8$)(C$_8$H$_9$)(dmpe) starting with 10.0 g of [Li(THF)$_4$]$^+$[Ta(C$_8$H$_8$)$_3$]$^-$, 2.5 g of dmpe, and 0.95 ml of CF$_3$CO$_2$H; yield 0.45 g.

See Figure 3 for its 220-MHz ^{1}H NMR spectrum. Its physical and spectroscopic properties are identical with Nb(C$_8$H$_8$)-(C$_8$H$_9$)(dmpe) in all respects and its identity thereby established.

18. Preparation of Nb(C$_8$H$_8$)[C$_8$H$_8${C(C$_6$H$_5$)$_3$}](dmpe). K$^+$[Nb(C$_8$H$_8$)$_3$]$^-$ (5.0 g), [(C$_6$H$_5$)$_3$C]$^+$BF$_4$$^-$ (4.0 g), and 5.0 g of dmpe were refluxed in 150 ml of THF with stirring for 1 h. The solution was filtered and the filtrate was stripped to a red syrup. This was dissolved in 50 ml of toluene and filtered. A small amount of hexane was added and the solution stood several days at room temperature. The orange precipitate was filtered off, washed with toluene, and dried in vacuo; yield 1.7 g (34%).

Anal. Calcd for C$_{41}$H$_{47}$P$_2$Nb: C, 70.89; H, 6.82. Found (crude sample): C, 68.67; H, 6.91.

19. Dimerization of Ethylene by Ta(C$_8$H$_8$)(CH$_3$)$_3$. A solution of Ta(C$_8$H$_8$)(CH$_3$)$_3$ (165 mg) in 50 ml of benzene in a 100-ml stainless steel shaker tube was pressurized to 50 atm C$_2$H$_4$ at 90 °C and shaken 4 h. Three liters of gas were collected, analyzed by mass spectroscopy, and found to contain ca. 5% 1-butene. The major component in the C$_6$H$_6$ solution was 1-butene (ca. 5%).

Line Shape Calculations. NMR line shapes were calculated using the density matrix method to first order and a two-site one-spin mode.^{7a} The chemical shift difference between the two C$_8$H$_8$ resonances, which varied slightly with temperature, was measured in the region below coalescence and extrapolated to higher temperatures. $\Delta G^{\ddagger}$ values were obtained from a standard Arrhenius plot. Those for the Nb compounds are less accurate due to peak broadening at higher temperatures, believed to be the result of coupling to ^{93}Nb.

Cell and Intensity Data. Crystals of Nb(C$_8$H$_8$)[C$_8$H$_8$-(C$_6$H$_5$)][(CH$_3$)$_2$AsC$_6$H$_4$As(CH$_3$)$_2$], recrystallized from toluene, are monoclinic with a = 8.981 (16), b = 31.930 (26), c = 12.177

Table III. Final Positional and Thermal Parameters[a]

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Nb	0.00853 (27)	0.33751 (7)	0.60849 (26)	98 (4)	60 (3)*	175 (4)	2 (1)	78 (3)	−1 (1)
As(1)	−0.07870 (37)	0.36167 (9)	0.38908 (35)	115 (6)	79 (4)*	183 (5)	−1 (1)	81 (5)	−1 (1)
As(2)	−0.22162 (38)	0.28432 (9)	0.50242 (37)	132 (6)	63 (4)*	199 (6)	−1 (1)	92 (5)	0 (1)
C(1)	−0.2884 (32)	0.3426 (9)	0.3086 (28)	115 (56)	11 (4)	113 (35)	8 (13)	47 (40)	−10 (9)
C(2)	−0.3510 (40)	0.3083 (9)	0.3588 (25)	183 (72)	13 (4)	104 (38)	−24 (14)	76 (45)	−9 (10)
C(3)	−0.4985 (43)	0.2958 (9)	0.3085 (33)	152 (69)	9 (4)	163 (43)	−8 (15)	61 (45)	4 (12)
C(4)	−0.5827 (39)	0.3146 (12)	0.2111 (34)	195 (74)	13 (5)	160 (46)	−7 (16)	66 (51)	−6 (12)
C(5)	−0.5315 (44)	0.3471 (11)	0.1596 (28)	274 (84)	11 (5)	97 (42)	6 (15)	30 (50)	−3 (12)
C(6)	−0.3811 (43)	0.3609 (10)	0.2179 (32)	104 (67)	12 (5)	163 (42)	−14 (15)	6 (43)	−5 (12)
C(7)	0.0190 (42)	0.3357 (10)	0.2782 (31)	355 (83)	15 (5)	194 (50)	−1 (16)	171 (55)	−20 (13)
C(8)	−0.0825 (36)	0.4199 (9)	0.3411 (29)	235 (69)	13 (4)	192 (47)	7 (14)	92 (48)	33 (12)
C(9)	−0.1821 (34)	0.2299 (9)	0.4327 (31)	195 (62)	10 (4)	256 (52)	1 (12)	91 (48)	−29 (12)
C(10)	−0.3670 (35)	0.2648 (9)	0.5887 (32)	215 (66)	11 (4)	319 (59)	−18 (13)	218 (53)	−5 (13)
C(11)	−0.2434 (37)	0.4940 (11)	0.6378 (43)	129 (62)	14 (6)	141 (57)	−4 (14)	71 (55)	−13 (16)
C(12)	−0.2579 (47)	0.5132 (14)	0.7304 (43)	298 (98)	24 (8)	211 (73)	1 (21)	106 (72)	19 (19)
C(13)	−0.3254 (51)	0.5602 (13)	0.7126 (56)	279 (99)	14 (6)	407 (109)	28 (18)	189 (92)	−33 (22)
C(14)	−0.3826 (59)	0.5743 (18)	0.6072 (51)	123 (92)	21 (10)	311 (93)	5 (24)	23 (73)	37 (23)
C(15)	−0.3573 (47)	0.5534 (12)	0.5285 (45)	205 (72)	8 (5)	295 (79)	1 (15)	134 (61)	12 (15)
C(16)	−0.2893 (41)	0.5137 (13)	0.5457 (34)	169 (68)	16 (7)	120 (47)	−7 (16)	37 (48)	2 (14)
C(21)	−0.2255 (33)	0.3732 (9)	0.5966 (29)	141 (56)	9 (4)	114 (39)	−5 (11)	69 (41)	0 (10)
C(22)	−0.1641 (43)	0.3568 (9)	0.7071 (38)	176 (76)	9 (4)	197 (56)	−14 (14)	156 (58)	−14 (13)
C(23)	−0.0169 (42)	0.3629 (9)	0.7823 (27)	140 (66)	12 (4)	105 (40)	−2 (14)	49 (45)	−2 (10)
C(24)	0.0986 (38)	0.3855 (10)	0.7520 (33)	140 (71)	11 (5)	174 (50)	7 (14)	5 (50)	−20 (12)
C(25)	0.0771 (33)	0.4091 (8)	0.6473 (32)	167 (61)	7 (4)	196 (49)	11 (12)	127 (46)	−2 (11)
C(26)	−0.0565 (33)	0.4372 (8)	0.5989 (28)	117 (55)	8 (4)	190 (43)	15 (13)	77 (42)	−12 (10)
C(27)	−0.1716 (32)	0.4498 (9)	0.6614 (31)	132 (54)	6 (4)	201 (53)	2 (12)	80 (46)	16 (12)
C(28)	−0.2216 (31)	0.4192 (9)	0.5713 (30)	83 (55)	5 (4)	224 (50)	−14 (11)	63 (42)	−9 (12)
C(31)	0.2723 (38)	0.3307 (9)	0.5799 (30)	221 (62)	18 (5)	180 (41)	54 (14)	176 (45)	19 (11)
C(32)	0.1754 (37)	0.2882 (10)	0.5714 (35)	115 (65)	9 (5)	319 (54)	49 (15)	−43 (50)	−31 (14)
C(33)	0.1301 (38)	0.2723 (9)	0.6732 (39)	146 (61)	9 (4)	245 (46)	−7 (12)	113 (54)	16 (14)
C(34)	0.1551 (46)	0.2802 (11)	0.7693 (36)	306 (84)	13 (5)	130 (42)	4 (15)	74 (56)	−12 (13)
C(35)	0.2657 (54)	0.2961 (12)	0.8539 (35)	303 (83)	12 (5)	237 (55)	19 (16)	192 (61)	15 (13)
C(36)	0.3950 (52)	0.3177 (12)	0.8660 (32)	456 (96)	20 (6)	113 (48)	44 (18)	150 (57)	27 (13)
C(37)	0.4515 (39)	0.3407 (11)	0.7922 (38)	155 (71)	22 (5)	125 (47)	44 (15)	−83 (54)	−35 (14)
C(38)	0.3977 (41)	0.3479 (10)	0.6726 (40)	90 (70)	14 (5)	275 (52)	−12 (15)	94 (52)	−29 (14)

[a] The estimated standard deviations here and in other tables are given in parentheses. The anisotropic temperature factor is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Temperature factors are $\times 10^4$ except for those followed by asterisks which are $\times 10^5$.

(7) Å, and $\beta = 106.97$ (8)°. The $P2_1/c$ space group was established from the systematic extinctions $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$. The calculated density for four molecules per cell is 1.32 g/cm³; we could not obtain an experimental density.

Crystals were mounted in sealed capillaries in a nitrogen-filled drybox. None of the many examined was entirely satisfactory; they diffracted poorly and gave broad peaks. We collected data on a prismatic crystal 0.10 × 0.21 × 0.34 mm using a Picker four-circle automatic diffractometer. Nickel-filtered Cu radiation (λ 1.5418 Å) was used to measure 2906 reflections out to 90° 2θ including the $0kl$ and $0k\bar{l}$ data which were averaged. The θ(crystal)-2θ(counter) technique was used to scan each reflection at 2°/min over 3.4° plus an increment due to the wavelength dispersion. Backgrounds (20 sec) were measured before and after each scan.

Data were corrected for a decline in intensity with time (maximum correction = 7% in F_o) and for absorption effects (six planes defined the crystal). The linear absorption coefficient for Cu Kα radiation is 56.6 cm⁻¹ and the minimum and maximum calculated transmission factors are 0.39 and 0.66, respectively. Structure factor errors were estimated as before[7b] and given zero weight in the refinement to reflections with $F < \sigma(F_o)$.

Structure Solution and Refinement. The structure was solved by "heavy-atom" techniques starting with the Nb atom located on a Patterson map. The R value ($\Sigma||F_o| - |F_c||/\Sigma|F_o|$) was 0.33 for the 1863 strongest reflections in a model including the Nb and As atoms. Remaining nonhydrogen atoms were added in steps. Hydrogen atom contributions were added in their calculated positions. For the methyl hydrogens, tetrahedral sets (C-H = 1.0 Å, B = 6.0 Å²), which best fit the electron density difference map, were chosen.

Final refinements were done in two parts: (a) the scale factor and all the parameters for the Nb, two As, C(1)-C(6) benzene, C(7)-C(10) methyl, and C(31)-C(38) cyclooctatetraene atoms; (b) the scale factor and all the parameters for the Nb, two As,

C(7)-C(10) methyl, C(11)-C(16) benzene, and C(21)-C(28) bicyclooctadienyl atoms. The final R values for the 2201 reflections with $F > \sigma(F)$ are 0.132 for R and 0.141 for R_w, $[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

The final electron density difference map was examined closely since the final R value is relatively large for this type of molecule. The map was acceptably clean in the region of the molecule except for peaks of 1.7 and 1.1 e/Å³ in the immediate vicinity of the Nb and As atoms. We feel these are associated directly with these atom positions and/or their thermal parameters. Residual electron density at ½0½ and the symmetry equivalent ½½0 site, however, almost certainly is due to toluene. The maximum observed peak was 1.6 e/Å³, but there were many very broad, smaller peaks. The ½0½ and ½½0 positions have $C_i(\bar{1})$ point symmetry so the toluene molecule must be disordered. Electron density difference maps were calculated in general projections through what appeared to be the most dense planes in hope that the disorder involved only two orientations. However, the results of this effort suggested a minimum of four orientations.

We next tried rigid-body least-squares techniques. One disordered toluene molecule, with and without varying the group isotropic temperature factor, was placed at the ½0½ site and allowed to move in the regular refinement. Though the molecule remained at the ½0½ position, the refinement would not converge. Extensive calculations with a subset of the 70 worst-fitting reflections (assuming these would have large contributions from the toluene), again with and without varying the group temperature factor, also proved futile.

We examined the packing at the ½0½ site and found the closest hydrogen atom to be H(12) (3.84 Å) and the closest carbon atoms C(12) (4.46 Å) and C(13) (4.65 Å), i.e., the toluene can fit into the hole at ½0½ (and ½½0) in almost any orientation. We therefore feel the toluene, as many as ½ per Nb is not unreasonable, cannot be included in the model in any reasonable way. It is most likely responsible for the limited precision and accuracy of the re-

finement but we feel it does not significantly affect the results concerning the configuration of the complex itself.

Neutral atom atomic scattering factors were used.[8] The Nb and As scattering factors were corrected for the real and imaginary parts of the anomalous scattering[9] and the function $\Sigma w(|F_o| - |F_c|)^2$ was minimized in the refinement.[10]

The final positional and thermal parameters for the nonhydrogen atoms are given in Table III. The hydrogen atom positions are listed in Table IV. A list of observed and calculated structure factors is available.[11]

Results

Preparation of M(C₈H₈)R from MCl₅. The C_8H_8 dianion reacts smoothly with metal complexes containing halide ligands to give products in which C_8H_8 has replaced two halides. The metal is formally reduced by two electrons if the resulting C_8H_8 is nonplanar, for example[12] $[Ru(NBD)Cl_2]_n$ + $[K^+]_2[C_8H_8]^{2-}$ → 2KCl + $Ru(NBD)(\eta^6\text{-}C_8H_8)$, (NBD = bicyclo[2.2.1]hepta-2,5-diene), but arguably not reduced when it is planar. An intermediate case is now known, $[M(\eta^4\text{-}C_8H_8)(\eta^3\text{-}C_8H_8)_2]^-$ (M = Nb, Ta)[13], in which the metal's oxidation state cannot be unambiguously assigned.

Addition of 2 mol of $[K^+]_2[C_8H_8]^{2-}$ in THF to MCl₅ (M = Nb, Ta) in toluene at −78° followed by warming to room temperature gives a brown product whose ¹H NMR spectrum in CD_2Cl_2 at 0° (two singlets in a 1:1 ratio at τ 3.76 and 4.51) suggests it consists largely of a member of the $M(C_8H_8)_2L$ class (L = uninegative ligand; vide infra). It was not characterized further. Quite likely it is $Nb(C_8H_8)_2Cl$.

Addition of 1 mol of phenyllithium to the above reaction mixture at −78° gives a red-brown solution on warming to room temperature from which $Nb(C_8H_8)_2C_6H_5$ can be isolated in fair yield (ca. 40%). We isolated a second product,[13] $[Li(THF)_4]^+[Nb(\eta^4\text{-}C_8H_8)(\eta^3\text{-}C_8H_8)_2]^-$, in ca. 20% yield. An attempt to prepare $Ta(C_8H_8)_2(C_6H_5)$ analogously gave primarily $[Li(THF)_4]^+[Ta(\eta^4\text{-}C_8H_8)(\eta^3\text{-}C_8H_8)_2]^-$ and only ca. 1% isolated $Ta(C_8H_8)_2(C_6H_5)$.

Attempts to prepare $M(C_8H_8)_2(CH_3)$ (M = Nb or Ta) in a similar fashion again gave largely $[Li(THF)_4]^+[M(\eta^4\text{-}C_8H_8)(\eta^3\text{-}C_8H_8)_2]^-$ and low yields of $M(C_8H_8)_2(CH_3)$ contaminated with $M(C_8H_8)_2Cl$, even using a slight excess of methyllithium.

Another preparative method was soon sought since this one is clearly not as straightforward as we originally hoped.[14]

Preparation of M(C₈H₈)₂R from MRCl₄. A much cleaner and more successful preparation of $M(C_8H_8)_2R$ consists of adding 2 mol of $[K^+]_2[C_8H_8]^{2-}$ to MRCl₄.

$M(CH_3)Cl_4$ (M = Nb, Ta) complexes have recently been isolated[15] but are best prepared for our purposes in situ from $Nb(CH_3)_2Cl_3$[16] and NbCl₅ or $Ta(CH_3)_3Cl_2$[17] and 2TaCl₅ in toluene (ca. 95% $M(CH_3)Cl_4$ after ca. 1 h at 25 °C). Addition of 2 mol of $[K^+]_2[C_8H_8]^{2-}$ to solutions of $M(CH_3)Cl_4$ at −78 °C followed by warming to room temperature and standard work-up gives $M(C_8H_8)_2(CH_3)$. The $[M(\eta^4\text{-}C_8H_8)(\eta^3\text{-}C_8H_8)_2]^-$ complexes are not obvious side products using this method.

Addition of $Zn(C_6H_5)_2$ to TaCl₅ in toluene rapidly gives a gelatinous $ZnCl_2$ precipitate and a yellow solution which almost certainly contains $Ta(C_6H_5)_2Cl_3$; 0.5 mol additional $Zn(C_6H_5)_2$ gives a pale yellow solution containing $Ta(C_6H_5)_3Cl_2$. Addition of 1 or 2 mol of TaCl₅ respectively gives $Ta(C_6H_5)Cl_4$. Solutions of all three are thermally unstable and none has yet been isolated analytically pure. Addition of 2 mol of $[K^+]_2[C_8H_8]^{2-}$ to a solution of "$Ta(C_6H_5)Cl_4$" in toluene at −78 °C gives $Ta(C_8H_8)_2(C_6H_5)$ in fair yield. $Nb(C_8H_8)_2(C_6H_5)$ has not

Table IV. Hydrogen Atom Positions[a]

	x	x	z
H(3)	−0.546	0.271	0.342
H(4)	−0.697	0.304	0.173
H(5)	−0.599	0.360	0.084
H(6)	−0.343	0.388	0.184
H(12)	−0.220	0.499	0.815
H(13)	−0.324	0.579	0.779
H(14)	−0.447	0.601	0.590
H(15)	−0.391	0.567	0.447
H(16)	−0.275	0.499	0.475
H(21)	−0.277	0.353	0.529
H(22)	−0.236	0.339	0.738
H(23)	−0.013	0.350	0.864
H(24)	0.209	0.386	0.811
H(25)	0.157	0.405	0.604
H(26)	−0.041	0.459	0.543
H(27)	−0.151	0.438	0.745
H(28)	−0.301	0.430	0.497
H(31)	0.236	0.350	0.509
H(32)	0.151	0.271	0.497
H(33)	0.053	0.248	0.653
H(34)	0.064	0.274	0.802
H(35)	0.260	0.291	0.936
H(36)	0.476	0.320	0.950
H(37)	0.556	0.356	0.828
H(38)	0.457	0.370	0.642
H(7a)	0.119	0.352	0.278
H(7b)	−0.052	0.337	0.197
H(7c)	0.049	0.306	0.297
H(8a)	−0.120	0.422	0.252
H(8b)	0.023	0.433	0.366
H(8c)	−0.157	0.437	0.370
H(9a)	−0.069	0.225	0.444
H(9b)	−0.239	0.229	0.348
H(9c)	−0.222	0.205	0.470
H(10a)	−0.316	0.245	0.650
H(10b)	−0.461	0.250	0.533
H(10c)	−0.409	0.289	0.622

[a] The labels correspond to the carbon atoms to which they bond; all had fixed B's of 6.0 $Å^2$.

been prepared in an analogous manner, the original method gives acceptable yields, since attempts to prepare niobium-phenyl complexes analogous to those postulated for tantalum in toluene, ether, dichloromethane, or acetonitrile gave largely paramagnetic products which were not identified.

Preparation of Ta(C₈H₈)Me₃. The reaction of 1 mol of $[C_8H_8]^{2-}$ with $Ta(CH_3)_3Cl_2$ at −78 °C in toluene gives a second type of C_8H_8 complex, $Ta(C_8H_8)(CH_3)_3$, in high yield. The major by-product, $Ta(C_8H_8)_2CH_3$, predominates if the reaction is carried out at room temperature.

$Nb(C_8H_8)_2CH_3$ was the only readily identifiable product of the reaction between $Nb(CH_3)_3Cl_2$[18] and $[C_8H_8]^{2-}$ at −78 °C while reaction of $Ta[CH_2C(CH_3)_3]_3Cl_2$[19] and $Ta(C_6H_5)_3Cl_2$ with $[C_8H_8]^{2-}$ gave complicated product mixtures.

Properties and Structure. The $M(C_8H_8)_2R$ species are red-brown and moderately soluble in polar solvents like THF, CH_2Cl_2, and o-dichlorobenzene. They dissolve in aromatic hydrocarbons only slightly and essentially not at all in aliphatic hydrocarbons or diethyl ether. They do not sublime without decomposition. $Nb(C_8H_8)_2(C_6H_5)$ decomposes most easily, at about 100° in the solid state. All react rapidly with air and moisture, Ta complexes more so than Nb, and do not dissolve sufficiently in benzene for molecular weight studies. They decompose under conditions necessary to obtain a mass spectrum. For $Nb(C_8H_8)_2(C_6H_5)$ (source = 200 °C) only a weak peak at m/e 378 was found; the major, mass-measured peaks were consistent with formation of $C_8H_7(C_6H_5)$ (strongest), $C_8H_6(C_6H_5)_2$, $C_8H_8(C_6H_5)_2$, biphenyl, biphenylene, and benzene.

In contrast, $Ta(C_8H_8)(CH_3)_3$ is blue, dissolves in aromatic hydrocarbons, and sublimes at 100 °C and 1 μ without decomposition. It is monomeric in benzene (351 found, 330 calcd) and gives the parent ion in the mass spectrum (330.0810 found, 330.0787 calcd) which is weak (wt 9) vs. the 315.0587 (315.0553 calcd) peak (wt 47) and 299.0275 (299.0240 calcd) peak, the strongest (wt 77). One methyl group is lost first, then methane; the C_8H_8 ring apparently does not survive further.

We believe the $M(C_8H_8)_2R$ complexes have a monomeric structure analogous to $Zr(\eta^8-C_8H_8)(\eta^4-C_8H_8)(THF)$.[20] The ^1H NMR spectra (vide infra) are consistent with this proposal. Also, the reaction of $Nb(C_8H_8)_2(C_6H_5)$ (1.34 mmoles) with ca. 10 mmol of DCl (35% in D_2O) in THF gave 1.09 mmol of C_6H_5D along with C_8H_8, C_8H_7D, and $C_8H_8D_2$ (yields undetermined), consistent with C_6H_5 being bound directly to the metal. If one describes $\eta^8-C_8H_8$ as a dianion, then these complexes can formally be regarded as M^{3+} derivatives.

$Ta(C_8H_8)(CH_3)_3$ most likely contains a planar C_8H_8 ring and the three methyl groups opposite in a tripod-like fashion. It is therefore a coordinatively unsaturated complex with a 16 valence-electron count. Other possibilities, $Ta(\eta^6-C_8H_8)(CH_3)_3$ for example, are unlikely since one would not expect an early metal to prefer a lower valence-electron count than the maximum possible. Its physical properties (compared to those of $M(C_8H_8)_2R$) are characteristic of its more symmetric structure.

^1H NMR Spectra. All η^4-, η^6-, or $\eta^8-C_8H_8$ ligands on group 4 and 5 metals exhibit a single ^1H NMR resonance at room temperature. As yet there has been no report of slowing down η^4- or $\eta^6-C_8H_8$ "spinning" to a rate where separate proton resonances can be observed, a well-known phenomenon for many later metal complexes.[21] Slowing $\eta^8-C_8H_8$ would certainly be more difficult, probably on the order of slowing $\eta^5-C_5H_5$ or $\eta^6-C_6H_6$ "spinning", neither of which has been unambiguously demonstrated. Each type of C_8H_8 ligand exhibits a signal at a different chemical shift in the τ 3.5–5 region but no effort to distinguish bonding mode on this basis alone has been made.

At -10 °C the $M(C_8H_8)_2R$ spectra consist of two singlets in the τ 3.5–5 region and signals characteristic of C_6H_5 or CH_3, consistent with the $M(\eta^8-C_8H_8)(\eta^4-C_8H_8)R$ proposal. On raising the temperature of $Ta(C_8H_8)_2R$ samples in o-dichlorobenzene, the two C_8H_8 singlets broaden and coalesce to a single signal with weight 16 (see Figure 1). The process is reversible and unaffected by the presence of free C_8H_8. The R signals shift slightly but otherwise do not change; the half-height width of the methyl peak is about 1.5 Hz at all temperatures. At 100 °C $Ta(C_8H_8)_2(C_6H_5)$ decomposes slightly but $Ta(C_8H_8)_2(CH_3)$ does not in several hours.

The $Nb(C_8H_8)_2R$ spectra are similar with one exception; the methyl line width $Nb(C_8H_8)_2(CH_3)$ is also temperature dependent. For example, at 0 °C in CD_2Cl_2 it is 1.7 Hz; at 25° it is 2.7 Hz. At high temperatures (in o-dichlorobenzene) the coalesced C_8H_8 singlet is also broad and *continues* to broaden as the temperature increases. This broadening is not due to an exchange process but coupling to ^{93}Nb ($I = \frac{9}{2}$, 100% abundant,[22a] $Q = 0.2$–0.4[22c]). Also, $Nb(C_8H_8)_2(C_6H_5)$ decomposes significantly at higher temperature to give free C_8H_8 and an unidentified Nb species. Both decomposition and coupling to Nb limit as detailed an examination of the temperature dependent process which we feel must be analogous to that in the Ta complexes.

Interconversion of the η^8- and $\eta^4-C_8H_8$ rings most reasonably explains the temperature dependent $M(C_8H_8)_2R$ spectra, viz.
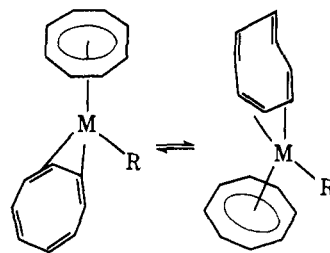
$\Delta G^{\ddagger}$ values (Table I) for the "ring-flipping" process in the four complexes differ by up to ca. 2 kcal/mol and are comparable to $\Delta G^{\ddagger}$ found for this process in $Ti(\eta^8-C_8H_8)(\eta^4-C_8H_8)$, the only other reported example.[23] Though limited, the data suggest the process takes place more readily for Ta than Nb and possibly also for R = CH_3 than R = C_6H_5. Two basic mechanistic possibilities are a step-wise process $[M(\eta^8-C_8H_8)(\eta^4-C_8H_8)R \rightarrow M(\eta^6-C_8H_8)(\eta^4-C_8H_8)R \rightarrow$ etc.] and a concerted process in which $\eta^8-C_8H_8$ smoothly converts to $\eta^4-C_8H_8$ and vice versa.

The ^1H NMR spectrum of $Ta(C_8H_8)(CH_3)_3$ is comparatively simple, two singlets in the ratio 8:9, consistent with its formulation and structure. The spectrum remains unchanged in the range -90 to 100 °C.

$M(C_8H_8)_2R$ and $Ta(C_8H_8)(CH_3)_3$ Adducts and Derivatives. Dmpe and diars (L-L) react instantly at room temperature with $Ta(C_8H_8)(CH_3)_3$ to give green adducts, $Ta(C_8H_8)(CH_3)_3(L-L)$. The ^1H NMR spectrum of $Ta(C_8H_8)(CH_3)_3(dmpe)$ (see Experimental Section) is unchanged at -90 °C or on addition of dmpe or C_8H_8 at 25 °C. The ^1H NMR spectrum of $Ta(C_8H_8)(CH_3)_3(diars)$ at -20 °C is similar except all resonances are singlets. At 25 °C we observe only one diars methyl and one Ta methyl resonance consistent with loss of the diars ligand; added diars also exchanges with coordinated diars at this temperature. The coupling of the two nonequivalent P nuclei in $Ta(C_8H_8)(CH_3)_3(dmpe)$ to C_8H_8 and the Ta methyl groups ($J_{H_8PP} = 1.1$ Hz, $J_{CH_3PP} = 3$ and 13 Hz, $J_{2CH_3PP} = 9.5$ and 11.5 Hz) suggest that both are bound to Ta; by analogy, the same is likely true of diars at -20 °C. The adducts' structures should be analogous and must have a plane of symmetry through the molecule. Two possible structures based on a pentagonal bipyramid, a geometry which has been found for some seven-coordinate Ta and Nb complexes,[24] are A and B. An $\eta^6-C_8H_8$, which would give

A   B   C

(M = Nb, Ta)
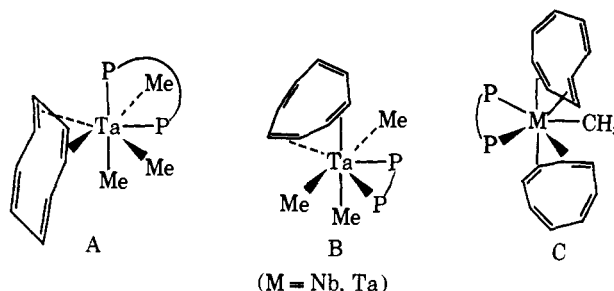
an 18 valence-electron count but also formally eight coordination, cannot be excluded, nor, in fact, can structures having η^3- or $\eta^5-C_8H_8$ (cf. $[Nb(\eta^4-C_8H_8)(\eta^3-C_8H_8)_2)]^-$).

One mole of dmpe adds to $M(C_8H_8)_2(CH_3)$ to give a similar adduct which can be observed by ^1H NMR at $-20°$. The apparently equivalent C_8H_8 rings and the methyl group are coupled to two nonequivalent P nuclei. Only two dmpe methyl group doublets suggest a C_2 axis consistent with (in the absence of intramolecular skeletal rearrangement), but not defining, a structure such as C (vide supra). The chemical shift of the M-methyl group is unexpectedly high, ca. τ 14. All resonances begin to broaden at

ca. 0 °C and free and coordinated dmpe exchange on the NMR time scale.

Both Ta(C$_8$H$_8$)(CH$_3$)$_3$ and Ta(C$_8$H$_8$)$_2$(CH$_3$) form monoadducts with P(CH$_3$)$_3$. Both can be isolated at room temperature. The ^{1}H NMR spectrum of Ta(C$_8$H$_8$)-(CH$_3$)$_3$[P(CH$_3$)$_3$] shows coordinated P(CH$_3$)$_3$ only at −70°; two of the three Ta–CH$_3$ groups are equivalent in the static structure. At −50 °C the C$_8$H$_8$ resonance is still a doublet (J = 1.4 Hz) but the two Ta–CH$_3$ sets are nearly collapsed; the Ta–CH$_3$ groups apparently begin to scramble intramolecularly before P(CH$_3$)$_3$ dissociates. The ^{1}H NMR spectrum of Ta(C$_8$H$_8$)$_2$(CH$_3$)[P(CH$_3$)$_3$] shows coordinated P(CH$_3$)$_3$ at −20°. As in M(C$_8$H$_8$)$_2$(CH$_3$)(dmpe), the two C$_8$H$_8$ rings are equivalent (J_{H_8P} = 1.3 Hz). The chemical shift of the M-methyl group is more normal, near TMS. Surprisingly, Nb(C$_8$H$_8$)$_2$(CH$_3$) does not form an adduct with P(CH$_3$)$_3$, even at −80 °C, as judged by the ^{1}H NMR spectra of equimolar mixtures in CD$_2$Cl$_2$.

M(C$_8$H$_8$)$_2$(C$_6$H$_5$) complexes show no evidence of forming adducts with dmpe or P(CH$_3$)$_3$ at −80 to +40 °C. The temperature-dependent spectra are characteristic of M(C$_8$H$_8$)$_2$(C$_6$H$_5$) in the absence of added ligand suggesting that not even a weak adduct, in which the C$_8$H$_8$ ligands would probably be equivalent (vide supra), can form. The simplest explanation is that the larger phenyl group prevents formation of a stable adduct. Electronic effects, on the surface, would appear to favor the opposite result, i.e., a stronger adduct with a metal having a relatively electron-withdrawing phenyl ligand. Yet that Ta(C$_8$H$_8$)$_2$(CH$_3$), but not Nb(C$_8$H$_8$)$_2$(CH$_3$), forms a P(CH$_3$)$_3$ adduct suggests that more subtle effects may be significant.

Apparent M(C$_8$H$_8$)$_2$(C$_6$H$_5$)(L-L) Adducts and Related Complexes. Apparent adducts between M(C$_8$H$_8$)$_2$(C$_6$H$_5$) and dmpe or diars do form on heating and can be isolated as orange to red crystals. The ^{1}H NMR spectrum of "Nb(C$_8$H$_8$)$_2$(C$_6$H$_5$)(dmpe)", however, is much more complex (Figure 2) than the spectra of the adducts described above. The signal due to dynamic C$_8$H$_8$ is a double doublet (J = 1.8 and 2.0 Hz) with an area of only eight protons, each methyl group on dmpe is unique, and at least six signals with area 1 can be seen (τ 4.64, 5.69, etc.). The spectra of the three other "adducts" are similar; Table II lists the ^{1}H NMR data for purposes of comparison. Apparently one C$_8$H$_8$ ring, or a related derivative, is static in a complex which has no symmetry. Only six of its eight proton resonances can be positively identified. A seventh, a multiplet, probably is located at τ 7.85 in "Nb(C$_8$H$_8$)$_2$(C$_6$H$_5$)(dmpe)" (see Figure 2) and at τ 7.97 in "Ta(C$_8$H$_8$)$_2$(C$_6$H$_5$)(diars)". The eighth probably falls under the L-L methyl resonances. In the diars "adducts" several are simplified since these protons are no longer coupled to P. Since proton chemical shifts in an asymmetric complex can vary widely[25] the shifts of the six or seven which can be seen cannot be used reliably to assign a structure to the static moiety.

Hydrolysis of "Nb(C$_8$H$_8$)$_2$(C$_6$H$_5$)(dmpe)" gave C$_8$H$_8$, C$_8$H$_{10}$ isomers, and C$_8$H$_9$(C$_6$H$_5$), all identified by GC/mass spectrometry. We found only traces of benzene. Hydrolysis of Nb(C$_8$H$_8$)$_2$(C$_6$H$_5$), on the other hand, does give 1 mol of benzene consistent with phenyl bound to the metal (vide supra). The phenyl ring in "M(C$_8$H$_8$)$_2$(C$_6$H$_5$)(L-L)" therefore must not be bound to the metal but probably to C$_8$H$_8$. All "adducts" of this type therefore should tentatively be reformulated as M(C$_8$H$_8$)[C$_8$H$_8$(C$_6$H$_5$)][L-L]. A crystal structure of Nb(C$_8$H$_8$)[C$_8$H$_8$(C$_6$H$_5$)](diars) (vide infra) shows this is the case.

Related Complexes Containing the C$_8$H$_8$E Ligands (E = H, D, C(C$_6$H$_5$)$_3$). The reaction of [M(C$_8$H$_8$)$_3$]$^-$ in the presence of dmpe in THF with E$^+$ (E = H, D, C(C$_6$H$_5$)$_3$) at

−78 °C gives 1 mol of C$_8$H$_8$ (see Experimental Section, preparation 16) and neutral complexes whose ^{1}H NMR spectra appear closely related to those of M(C$_8$H$_8$)[C$_8$H$_8$(C$_6$H$_5$)](L-L). However, the number of signals has approximately doubled (see Figure 3). For example, the dynamic C$_8$H$_8$ signals in Nb(C$_8$H$_8$)(C$_8$H$_9$)(dmpe) (τ 4.49 and 4.62 in C$_6$D$_6$ at 220 MHz) each have area 4 and are poor triplets ($J \approx 2$ Hz), eight dmpe methyl doublets can be rationalized, and there are two high-field triplet resonances (or a poor quartet) below TMS in C$_6$D$_6$ or above in CD$_2$Cl$_2$ (decomposes) or THF-d_8, and a profusion of weak resonances from ca. τ 4 to 10. The spectrum of Nb(C$_8$H$_8$)(C$_8$H$_8$D)(dmpe) is essentially identical except one or more of the C$_8$H$_8$D signals in the τ 7.5–8.0 region are simplified. Though we cannot be certain D is attached stereospecifically to the ring, we can at least conclude that the highest field signals observed in each complex of this type are *not* due to protons on the same nor probably on an adjacent carbon to which D is attached. We found a weak ν_{C-D} band in the infrared spectrum of Nb(C$_8$H$_8$)(C$_8$H$_8$D)(dmpe) at 2040 cm^{-1}.

The ^{1}H NMR spectrum of Nb(C$_8$H$_8$)[C$_8$H$_8$C-(C$_6$H$_5$)$_3$](dmpe) shows primarily a single dynamic C$_8$H$_8$ resonance (τ 4.95 in THF-d_8, a poor triplet, $J \approx 2$ Hz) with a second of the same type ~6 Hz upfield (220 MHz) with <10% the intensity of the first. The gross features, four dmpe methyl doublets and a high-field triplet with approximate area 1, show this species to be primarily one isomer containing a trace of a second. Though qualitatively similar, the spectrum does not by itself provide good evidence that this species is structurally analogous to M(C$_8$H$_8$)(C$_8$H$_9$)(dmpe) or M(C$_8$H$_8$)[C$_8$H$_8$(C$_6$H$_5$)]-[dmpe]. What it does suggest is that M(C$_8$H$_8$)(C$_8$H$_9$)(dmpe) is also probably an isomeric mixture.

The Structure of Nb(C$_8$H$_8$)[C$_8$H$_8$(C$_6$H$_5$)](diars). A crystal structure of a representative complex was undertaken in order to establish the structure of at least one compound.

The molecular structure shown in Figure 4 reveals a 2,3,4,5,6-η-8-phenylbicyclo[5.1.0]octadienyl, an η^4-C$_8$H$_8$, and a bidentate o-phenylene(bisdimethylarsine) ligand. The molecular has no special point symmetry. The most important interatomic distances and angles are shown in Figure 5 (idealized) while Table V lists some remaining distances and angles. Table VI lists least-squares planes and dihedral angles.

The bicyclic ligand bonds to Nb through C(21)–C(25) which lie in a plane (within 0.03 Å) 1.79 Å away. The average distance to each carbon (2.33 (2) Å) is slightly shorter than those found between Nb and η^5-C$_5$H$_5$ carbons (ca. 2.40 Å).[26] The C(21), C(25), C(26), C(28) plane makes an angle of 132.2° with the bonding plane and 114.1° with the C(26)–C(28) plane, the exo cyclopropyl ring. The C(26)–C(28) bond length (1.53 (4) Å) is normal. The phenyl group is planar and nearly orthogonal (86°) to the cyclopropyl ring. For calculation purposes C(21) and C(25) were assumed to be sp^2 hybridized; this places H(21) and H(25) about 0.7 Å away from the bonding plane toward the metal. Distances between H(16), H(26), and H(28) are short (Table V) but not unreasonable. H(27) lies 2.28 Å above the coordination plane.

The η^4-C$_8$H$_8$ ligand is bound to Nb through C(31)–C(34). The range of Nb–C bond lengths (2.31 (4)–2.72 (4) Å) is similar to the range found for η^4-C$_8$H$_8$ in [As(C$_6$H$_5$)$_4$][Nb(η^4-C$_8$H$_8$)(η^3-C$_8$H$_8$)$_2$] (2.342 (14)–2.683 (17) Å).[13] The angle between the C(31)–C(34) and the six-atom (C(31), C(34)–C(38)) planes (152.2°) is also similar to that in [Nb(C$_8$H$_8$)$_3$]$^-$ and to those in other η^4-C$_8$H$_8$ complexes.[13]
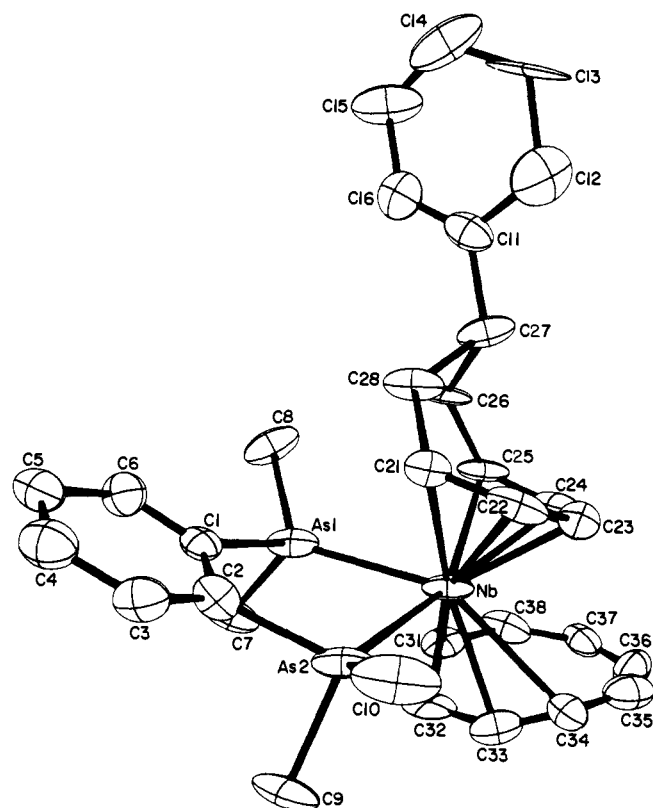
Figure 4. Molecular structure of Nb(η^4-C$_8$H$_8$)(2,3,4,5,6-*endo*-8-phenylbicyclo[5.1.0]octadienyl)[(CH$_3$)$_2$As-C$_6$H$_4$-As(CH$_3$)$_2$]. Hydrogen atoms are omitted and thermal ellipsoids plotted at the 30% level.

The one unusual feature about the diars geometry is the 154.9° angle between the Nb, As(1), As(2) plane and the C(1)–C(6) plane which is apparently caused by repulsion between the C(7) and C(9) methyl groups and η^4-C$_8$H$_8$. The As(CH$_3$)$_2$ planes are more nearly orthogonal to the *o*-phenylene ring (plane I, Table VI) than the NbAs$_2$ plane. The average Nb–As distance (2.682 (4) Å) is only slightly larger than Mo–As (2.62 Å) in [Mo(diars)$_2$(CO)$_2$I]$^+$I$^-$ (ref 27).

The interatomic C–C distances and angles are normal for the geometries involved. Several large errors prevent a meaningful detailed comparison with other compounds. The worst, C(33)–C(34) and C(12)–C(13), are probably associated with the disordered toluene problem (see Experimental Section). This is particularly true of the latter whose hydrogens make the shortest contacts with the disordered toluene. Their thermal behavior (see Figure 4) may also reflect these contacts.

The shortest intramolecular contacts are listed in Table V; some have received comment. The shortest intermolecular contacts are 2.72 Å for the C···H type [C(5)···H(36)] and 2.29 Å for H···H[H(15)···H(38)]. A significant feature of the packing is the random orientation of a toluene molecule at the ½0½ and ½½0 positions (vide supra).

In simple terms the molecule could be viewed as a tetrahedron with C$_8$ rings each occupying one ligand site (see Table V). The expected internal compensation for ligands involved yields a large CNT2–Nb–CNT3 angle (131.1°) in response to a small As–Nb–As angle (75.10°). Electronically the niobium achieves a full complement of 18 valence electrons.

Discussion

The Structure and C$_6$H$_5$ Migration. The crystal structure is the first of a complex containing a bicyclic[5.1.0]octadienyl ligand. Comparison of the ^{1}H NMR spectra of the four

Table V. Interatomic Distances and Angles (Supplement to Figure 5)[a]

	Interatomic Angles, deg		
As(1)–Nb–CNT2	109.7	C(21)–Nb–C(22)	34.9(12)
As(1)–Nb–CNT3	114.5	C(22)–Nb–C(23)	34.7(12)
As(1)–Nb–As(2)	75.1	C(23)–Nb–C(24)	35.2(11)
As(2)–Nb–CNT2	115.0	C(24)–Nb–C(25)	36.0(12)
As(2)–Nb–CNT3	95.8	C(31)–Nb–C(32)	38.5(10)
CNT2–Nb–CNT3	131.1	C(32)–Nb–C(33)	37.4(12)
		C(33)–Nb–C(34)	25.0(14)
Nb–As(1)–C(7)	120.0(10)	Nb–As(2)–C(9)	122.8(8)
Nb–As(1)–C(8)	123.4(9)	Nb–As(2)–C(10)	118.2(8)
C(7)–As(1)–C(1)	94.7(12)	C(9)–As(2)–C(2)	95.4(13)
C(8)–As(1)–C(1)	102.6(12)	C(10)–As(2)–C(2)	106.5(13)

	Intramolecular Contacts, Å		
As(1) · · · As(2)	3.27	H(25) · · · Nb	2.53
H(16) · · · H(26)	2.29	H(25) · · · H(31)	2.32
H(16) · · · H(28)	2.23	H(26) · · · H(28)	2.43
H(21) · · · Nb	2.51	H(26) · · · H(8c)	2.18
H(21) · · · As(2)	2.30	H(27) · · · H(12)	2.28
H(21) · · · C(2)	2.44	H(28) · · · H(8c)	2.31
H(22) · · · H(10c)	2.37	H(32) · · · H(9a)	2.40

[a]CNT denotes the atom centroids: CNT2 for atoms C(21)–C(25) and CNT3 for atoms C(31)–C(34).

Table VI. Least-Squares Planes[a]

Equations of Planes and Atom Deviations, Å

1. $-0.5299X + 0.6403Y + 0.5561Z - 1.098 = 0$
   C(1) –0.02, C(2) –0.01, C(3) 0.02, C(4) –0.01, C(5) –0.02, C(6) 0.03, As(1)[b] 0.04, As(2)[b] 0.09
2. $0.9043X + 0.4045Y + 0.1365Z - 3.377 = 0$
   C(11) –0.01, C(12) –0.03, C(13) 0.06, C(14) –0.05, C(15) 0.01, C(16) 0.02, C(27)[b] –0.04
3. $-0.4438X + 0.8081Y + 0.3874Z - 1.417 = 0$
   C(21) –0.01, C(22) 0.00, C(23) 0.03, C(24) –0.03, C(25) 0.02, C(26)[b] 0.99, C(27)[b] 2.15, C(28)[b] 1.01, H(27)[b] 2.28, Nb[b] –1.79, H(26)[b] 1.15, H(28)[b] 1.15, H(21)[b] –0.73, H(25)[b] –0.68
4. $0.8050X - 0.5396Y + 0.2466Z + 3.714 = 0$
   C(31) –0.01, C(32) 0.02, C(33) –0.03, C(34) 0.02, Nb[b] –2.03

Dihedral Angles, deg[c]

C(21)–C(25) C(21), C(25), C(26), C(28) } 132.2	C(31)–C(34) C(31), C(34)–C(38) } 152.2
C(21), C(25), C(26), C(28) C(26), C(27), C(28) } 114.1	Nb, As(1), As(2) C(1)–C(6) } 154.9
C(26), C(27), C(28) C(11)–C(16) } 86.0	

[a] The equations are based on the Cartesian coordinate system (a, b, c^*). [b] These atoms were not included in the plane calculation. [c] The dihedral angles are the angles between the planes, not plane normals.

complexes of this type (Table II) leaves little doubt that all have identical gross structural features.

The bicyclic C$_8$H$_9$ ligand has been postulated in several systems,[28] usually one in which a C$_8$H$_8$ ligand has been protonated; the cyclopropyl ring has always been assumed exo to the metal. The exo configuration found here suggests that this assumption has probably been correct while the endo phenyl group on the methylenic carbon atom is consistent with phenyl transfer from the metal to a C$_8$H$_8$ ring. This transfer might be compared to the migration of C$_6$H$_5$ from V[29] or C$_2$H$_5$ from W[30] to η^5-C$_5$H$_5$.

At least four forms of a C$_8$H$_8$ ligand resulting from protonation of C$_8$H$_8$ have been postulated (A–D).[28] Of the
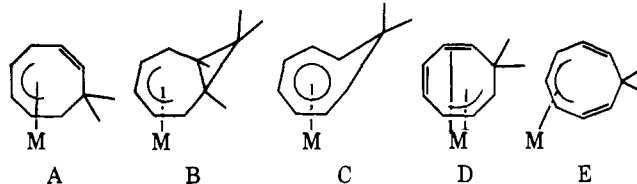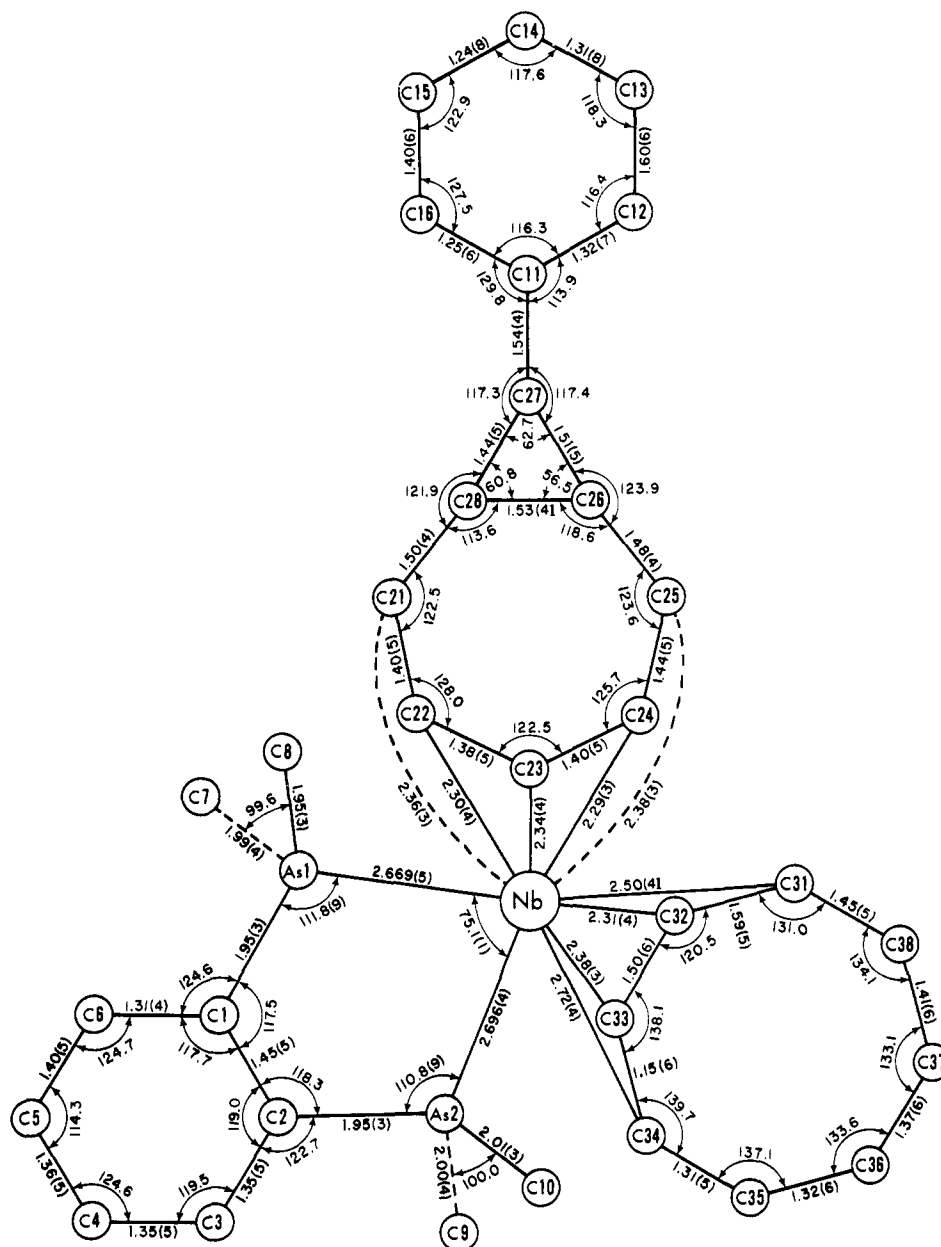
Figure 5. Idealized structure showing interatomic distances and angles. Unless specified the estimated errors in the angles are 3°.

five-electron donors, A, B, and D, examples where A → B and B → D are known, but not the reverse. If the relative energies of these forms hold also for $C_8H_8(C_6H_5)$ ligands on Nb or Ta then D is an unlikely intermediate in formation of the observed B. An intermediate E form is also possible since the process η^4-C_8H_8 (the second original C_8H_8 ligand) → η^6-C_8H_8 would maintain an 18 valence-electron count. The C form is rare and the least plausible stable intermediate to B though a transition state of this type at some point on route to B is reasonable.

Migration of C_6H_5 from the metal to the ring most likely does not require assistance from dmpe or diars except that their coordination prevents the reverse. It should be recalled that $M(C_8H_8)_2(C_6H_5)$ decomposes in solution near 100 °C, and an attempted mass spectrum of $Nb(C_8H_8)_2(C_6H_5)$ gave (inter alia) $C_8H_7(C_6H_5)$, $C_8H_6(C_6H_5)_2$, and $C_8H_8(C_6H_5)_2$. In contrast, solutions of $M(C_8H_8)_2(CH_3)$ do not decompose readily, and decomposition of solid $Nb(C_8H_8)_2(CH_3)$ at ~200 °C in vacuo gave only C_8H_8, C_8H_{10}, and C_8H_{12} (ca. 8:4:1) as the volatile products. Heating $M(C_8H_8)_2(CH_3)$ and dmpe in THF or benzene for

several days destroys the complex but no products could be identified in situ or isolated. $Ta(C_8H_8)(CH_3)_3(dmpe)$ is likewise quite stable, it is unchanged after heating to 100 °C for 24 h in C_6D_6. Apparently, therefore, C_6H_5 transfers to C_8H_8 more readily than CH_3, not a surprising result in view of the fact that electrophiles readily attack C_8H_8 ligands and C_6H_5 is quite likely more electrophilic than CH_3. Some parallel with the transfer of a Pd-aryl group to an olefin[31] might be drawn here. We should note, however, that refluxing 3.0 g of $Ta(C_8H_8)(CH_3)_3$ in toluene in the presence of 1 ml of C_8H_8 for ~3.5 days yields about a dozen volatile organic products consisting of C_8H_x, $C_8H_y(CH_3)$, and $C_8H_z(CH_3)_2$; only $Ta(C_8H_8)_2(CH_3)$ could be positively identified (by ^1H NMR) in the tar-like residue.

The Products of Electrophilic Attack on $[Nb(C_8H_8)_3]^-$. Electrophilic attack (E^+) on a C_8H_8 ligand may occur directly to give an exo-C_8H_8E ligand, or at the metal followed by a migration analogous to that just discussed to give the $endo$-C_8H_8E ligand; both are known for E = H or D.[28] Trityl ($C(C_6H_5)_3^+$) is often used to abstract H^- from

a hydrocarbon ligand but rarely adds to a ligand to give the analogue of a protonation product. One might expect it would be less likely to attack the metal, since it is so large, and should add exo to C_8H_8. However, electron transfer to give $C(C_6H_5)_3$ may be facile and cannot be ruled out as a mechanistic possibility, the result of which overall may be indistinguishable from an electrophilic attack analogous to protonation.

Three questions concerning the products of electrophilic attack, $M(C_8H_8)(C_8H_8E)(dmpe)$, are: (i) what is the gross structure of C_8H_8E; (ii) is E exo or endo; and (iii) are isomers due to different C_8H_8E forms (i.e., A, B, etc., vide supra), or to the ways a single type C_8H_8E is bound in an asymmetric complex? Answers to these questions might be provided by infrared or NMR, albeit not without considerable ambiguity.[32] The only conclusion which we feel is justified at this time bears on (iii), and that is, isomers, whatever they may be, apparently do not interconvert readily, or if they do, one is not thermodynamically favored over the other. For example, a sample of $Nb(C_8H_8)(C_8H_9)(dmpe)$ was heated in THF in a sealed vial at 100 °C for 16 h; the recovered crystalline product was the identical isomeric mixture. The fact that primarily one $Nb(C_8H_8)[C_8H_8\{C(C_6H_5)_3\}](dmpe)$ isomer is found may indicate that the large $C(C_6H_5)_3$ group causes one isomer to be kinetically and/or thermodynamically favored.

The Adducts. The formation of PMe_3 and dmpe adducts with $M(C_8H_8)_2(CH_3)$ and $Ta(C_8H_8)(CH_3)_3$ suggests that the cyclooctatetraene ligand can behave as a "protecting" group which readily decreases the extent of its bonding to the metal during the process of, or perhaps in order to allow, ligand attack at the metal center. We might view the process of η^8- and η^4-C_8H_8 interconversion in the $M(\eta^8$-$C_8H_8)(\eta^4$-$C_8H_8)R$ complexes as an intramolecular version of this phenomenon, i.e., the "incoming ligand" is simply the nonbonded portion of η^4-C_8H_8.

Some parallels can be drawn between adduct formation and the ability of these complexes to function as catalysts, or, perhaps more accurately, catalyst precursors, for the oligomerization of ethylene to primarily 1-butene (see Experimental Section). $Ta(C_8H_8)(CH_3)_3$ ($C_6H_6/90$ °C/50 atm/4 h) and $Nb(C_8H_8)_2(C_6H_5)$ (THF/90 °C/50 atm/4 h) are both mildly active yet, surprisingly, no 1-butene was found using $Ta(C_8H_8)_2(CH_3)$ in toluene. More extensive studies along these lines are clearly needed before we can relate accurately the η^8-$C_8H_8 \rightarrow$ (e.g.) η^6-C_8H_8 or ligand transfer processes with reactions at the metal center. Significantly, however, $Nb(C_8H_8)(C_8H_9)(dmpe)$ does not effectively catalyze ethylene oligomerization (in C_6H_6). Here analogous low-energy processes for creating sites at the metal center are not possible.

Conclusion

The η^8-C_8H_8 ligand shows some potential as a "labile" ligand in the sense that it can decrease its coordination number to allow reagents access to the metal. Ligand transfer from the metal to C_8H_8 is another means by which coordination sites can be created. A crystal structure of an example of the latter shows that the 2,3,4,5,6-η-endo-8-phenylbicyclo[5.1.0]octadienyl ligand is one viable type of octadienyl ligand which can be found in Nb and Ta complexes. Electrophilic attack on C_8H_8 does not necessarily produce a similar octadienyl ligand.

References and Notes

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type show a weak peak at 1650–60 cm⁻¹ which we ascribe to a mode involving one or both C_8 ligands. The 1550–60-cm⁻¹ peak for compounds of the $M(C_8H_8)_2(C_6H_5)$ type is probably a phenyl mode since it is absent in the spectrum of $M(C_8H_8)_2(CH_3)$. The 1590–1600-cm⁻¹ peak for the $M(C_8H_8)[C_8H_8(C_6H_5)](L-L)$ species might suggest that they are unique yet that this peak is a C_8-phenyl combination mode seems quite probable.

Crystal and Molecular Structure of an N-Substituted Porphyrin, Chloro(2,3,7,8,12,13,17,18-octaethyl-N-ethylacetatoporphine)cobalt(II)

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Abstract: The crystal and molecular structure of the title compound were determined from three-dimensional x-ray crystallographic data, and refined to $R = 0.041$ for 2417 reflections by least-squares methods. The monoclinic unit cell, space group $P2_1/n$, has dimensions $a = 15.214$ (4) Å, $b = 17.020$ (7) Å, $c = 14.760$ (2) Å, and $\beta = 93.59$ (1)° for $Z = 4$. The cobalt(II) atom is 5-coordinate, even though one of the bonds is much weaker than the other four, with the substituted nitrogen atom 0.4 Å farther from the cobalt atom than are the other nitrogen atoms. The deviation of the porphyrin ring from planarity is increased markedly by the coordination; the ring of the substituted nitrogen atom is deviated 44° from the mean plane of the other three nitrogen atoms. The chlorine atom leans decidedly toward the substituted nitrogen atom. The side chain is essentially planar, and no inter- or intramolecular oxygen coordination is found.

A great deal of interest has been shown recently in the porphyrins,[2-17] in great part because of their biological importance in such compounds as vitamin B_{12}. In addition to normal porphyrins[5-8] and their metal complexes,[9-11] a wide variety of nonplanar porphyrins has been studied, including N-substituted examples,[12-14] protonated cations,[15] partially saturated derivatives,[16] and nonplanar forms of the normal varieties.[17]

This investigation deals with octaethylporphyrin which has an ethyl acetate group substituted on one of the nitrogen atoms. (See Figure 1.) The effect of N-substitution on nonmetallo octaethylporphyrin (OEP) has been shown to have a significant effect on the normal planarity of the macrocycle.[12] The effect of coordination of a great variety of metal ions on such macrocycles is of great interest, because the normal square planar or octahedral geometries cannot be expected due to steric interference of the carbon atom substituted on the nitrogen of the macrocycle. It was of interest to determine if the carboxylate group of the substituted side chain could coordinate to the central metal intra- or intermolecularly. Cobalt(II) complexes of porphyrins which are not N-substituted are normally found to be pyramidal or octahedral;[9] the substitution on the nitrogen atom causes the present complex to be different in a variety of ways.

Experimental Section

The compound was prepared by Mr. D. Ward and Professor A. W. Johnson,[18] University of Sussex, by standard methods. Crystal data:[19] $C_{40}H_{51}ClCoN_4O_2$; M = 714.24; monoclinic; $a = 15.214$ (4), $b = 17.020$ (7), $c = 14.760$ (2) Å; $\beta = 93.59$ (1)°; $U = 3814.5$ Å³; $Z = 4$; $F(000) = 1516$; $d_{calcd} = 1.24$, $d_{obsd} = 1.24$ (1) g cm⁻³; space group $P2_1/n$ (nonstandard); Mo Kα_1 (λ 0.70926 Å) radiation for cell dimension and intensity measurements, μ(Mo Kα) = 5.76 cm⁻¹.

Systematic absences on Weissenberg and precession photographs lead to the conclusion that the space group is $P2_1/n$, a nonstandard setting of $P2_1/c$. Preliminary cell dimensions were measured from precession photographs using Mo Kα radiation and

were subsequently adjusted by least-squares refinement of the setting angles of 12 reflections measured on a Hilger and Watts Y 290 four-circle diffractometer using Mo Kα_1 radiation (λ 0.70926 Å) with a graphite crystal monochromator. A crystal measuring $0.70 \times 0.18 \times 0.17$ mm was mounted with the c axis almost coincident with the ϕ axis of the diffractometer. Intensity measurements were made by the θ–2θ step-scan procedure, each reflection being scanned in 72 1-sec steps of 0.01° about $2\theta_{calcd}$. The peak profiles were somewhat broad, with a slight shoulder to one side of the peak maximum. Stationary background counts were measured for 36 sec at each end of the scan range. The intensities of the (020), (110), and (101) reflections were checked every 100 reflections to monitor crystal and electronic stability. No deviations greater than statistical were observed. Intensities were collected for reflections with θ (Mo Kα) $\leq$ 20°. Out of a total of 4081 reflections, there were 2625 with $I \geq 3\sigma(I)$, of which 2417 were used as unique. These were corrected for Lorentz and polarization effects, but correction for absorption was not necessary.

Structure Analysis. The position of the cobalt atom was determined from a three-dimensional Patterson synthesis. A structure factor calculation based on this position yielded $R = 0.507$. The coordinates of the other nonhydrogen atoms were obtained from three subsequent difference Fourier and least-squares cycles. Least-squares refinement of positional and isotropic thermal parameters, with the program CRYLSQ[20] in the blocked mode gave $R = 0.094$. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F^2)$. Scattering factors for hydrogen[21] and for other atoms[22] were taken from standard sources. Anomalous dispersion factors $\Delta f'$ and $\Delta f''$ for Co and Cl were taken from ref 23. Anisotropic refinement of Co and Cl caused the decrease of R to 0.086. The locations of the 24 nonmethyl hydrogen atoms were calculated; the 27 methyl hydrogen atoms could not be located on a difference map at this point, and so were not included. With the 24 hydrogen atoms included, a structure factor calculation yielded an R factor of 0.077. Because the difference map showed residual effect consistent with anisotropic behavior of the ethylacetato chain (C(37)–C(40), O(1), and O(2)), anisotropic refinement was performed, causing R to decrease to 0.068. A peak search routine at this point yielded positions of at least one or two hydrogen atoms on each terminal carbon of the eight ethyl groups on the macrocycle. Peak heights for the hydrogen atoms ranged from 0.4 to 0.7