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Synthesis, Characterization, and Catalytic Behavior of a Ruthenium(II) Tetraazaannulene Complex

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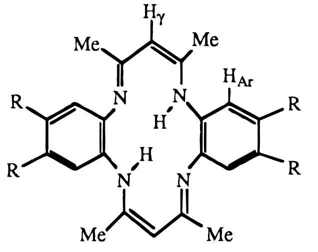
Introduction

Recent synthetic and catalytic developments in the area of metal complexes bearing azaannulene supporting ligation have focused on representative and early transition metal elements.[1−3] Few examples of complexes bearing this supporting ligation exist for middle transition metal systems.[1,4] Although related to porphyrins, the base ligand (H_2Me_8taa) possesses a saddle-shape[5] configuration which differentiates it from planar porphyrins. In view of the rich chemistry exhibited by complexes bearing porphyrin and porphyrin-like ligands, we became interested in examining the chemistry of complexes bearing this tetraazaannulene ligand in order to compare their structural features and reactivities with those of porphyrin relatives.



R = H (H_2Me_4taa) or Me (H_2Me_8taa)

Experimental Section

General Considerations. All manipulations involving organoruthenium complexes were performed under inert atmospheres of argon or nitrogen using standard high vacuum or Schlenk tube techniques, or in a Vacuum/Atmospheres glovebox containing less than 1 ppm oxygen and water. Solvents were dried and distilled under dinitrogen before use employing standard drying agents.[6] NMR spectra were recorded using a Varian Gemini 300 MHz spectrometer. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY.

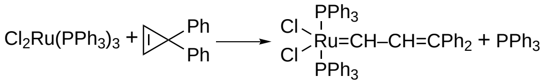
Synthesis of 1. In a typical synthetic procedure, 0.45 g (0.47 mmol) of $Ru(PPh_3)_3Cl_2$, 0.20 g (0.47 mmol) of Li_2(omtaa),[3b] and 10 mL of THF were charged in a 25 mL flask of a swivel frit assembly in an inert atmosphere glovebox. This apparatus was subsequently brought out of the glovebox and attached to a high vacuum line. The solution color immediately became dark green. After 4 h of stirring, 3 mL of pentane was added to aid the precipitation of LiCl; the solution was then filtered, and the solvent was removed under vacuum. The solid residue then was washed with small amount of diethyl ether until no brown or purple color remained and then washed with 3 × 1 mL pentane and dried under vacuum, giving a dark green powder, yield 0.48 g (98%). Scale up to gram quantities is succesful with similar percentage of isolated yields. Analytical data for **1**: ^{1}H-NMR (300 MHz, THF-d_8, 25 °C): δ 1.80 (s, 12 H, CH_3- on annulene ring); δ 2.03 (s, 12 H, CH_3- on benzyl groups); δ 4.55 (s, 2 H, protons of annulene ring); δ 5.85 (s, 4 H, protons of benzyl groups); δ 7.22 (m, 30 H, protons of triphenyl phosphines). ^{31}P{^{1}H}-NMR (300 MHz, THF-d_8, 25 °C, H_3PO_4 as internal reference): δ 131.9 (trans triphenyl phosphines). Anal. Calcd for RuP_2N_4 $C_{62}H_{60}$: C, 72.71; H, 5.90; N, 5.47. Found: C, 72.49; H, 5.63; N, 5.02.

Results and Discussion

Developments of the chemistry of middle transition metal complexes bearing the tetraazaannulemne ligation have been impeded by the low yield preparation reported in the literature.[4b,7]

$$H_2Me_4\text{taa} + Ru_2(OAc)_4 + 2PMePh_2 \xrightarrow[\Delta,\ 20\ h]{EtOH} (Me_4\text{taa})Ru(PMePh_2)_2 \quad (1)$$

Furthermore, in view of the nature of the phosphine ligand present in eq 1, which turns out to be relatively strongly bound to ruthenium, subsequent ligand substitutions have proven difficult.[4b] The high yield synthetic route presented here was formulated with the help of recent thermochemical results focusing on organoruthenium complexes[8] and the recently demonstrated labile nature of the $Ru-PPh_3$ bond in $Cl_2Ru(PPh_3)_3$ reported by Grubbs and co-workers.[9]



(2)

The ruthenium annulene synthesis is achieved by reacting $Cl_2Ru(PPh_3)_3$ with the $Li_2(Me_8$taa) salt recently described[3] and utilized by Jordan and co-workers[3b] in their early transition metal-annulene work.

$$ZrCl_4(THF)_2 + Li_2Me_8\text{taa} \rightarrow (Me_8\text{taa})ZrCl_2 + 2LiCl \quad (3)$$

By a related salt elimination/ligand displacement reaction, the title complex is isolated in >95% yield on a multigram scale

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(1) For a review of this topic see: Cotton, F. A.; Czuchajowska, J. *Polyhedron* **1990**, *9*, 2553−2566.

(2) For representative element complexes see: (a) Cannadine, J. C.; Errington, W.; Moore, P.; Wallbridge, M. G. H.; Nield, E.; Fenn, D. *J. Organomet. Chem.* **1995**, *486*, 237−242. (b) Guillard, R.; Zrineh, A.; Tabard, A.; Courthaudon, L.; Han, B.; Ferhat, M.; Kadish, K. M. *J. Organomet. Chem.* **1991**, *401*, 227−243. (c) Kuroki, M.; Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1987**, *109*, 4737−4738.

(3) For zirconium complexes see: (a) Giannini, L.; Solari, E.; De Angelis, S.; Ward, T. R.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1995**, *117*, 5801−5811. (b) Uhrhammer, R.; Black, D. G.; Gardner, T. G.; Olsen, J. D.; Jordan, R. F. *J. Am. Chem. Soc.*, **1993**, *115*, 8493−8494.

(4) (a) Cotton, F. A.; Czuchajowska, J. *J. Am. Chem. Soc.* **1991**, *113*, 3427−3431. (b)Cotton, F. A.; Czuchajowska, J. *Polyhedron* **1990**, *9*, 1221−1224. (c) Cotton, F. A.; Czuchajowska, J. *Polyhedron* **1990**, *9*, 1217−1220. (d) Warren, L. F.; Goedken, V. L. *Chem. Commun.* **1978**, 909−910 and references cited.

(5) (a) Nolan, S. P.; Mahler, C. H.; Stevens, E. D. *Acta Crystallogr.* **1995**, *C51*, 1855−1857. (b) Goedken, V. L.; Weiss, M. C. *Inorg. Synth.* **1980**, *20*, 115−119.

(6) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: New York, 1988.

(7) An alternative synthetic route employing the free annulene ligand and metal chlorides in a basic medium has also lead to the isolation of transition metal tetraazaannulene complexes: (a) Edema, J. J; Gambarotta, S.; van der Sluis, P.; Smeets W. J. J.; Spek, A. L. *Inorg. Chem.* **1989**, *28*, 3782−3784. (b) Mandon, D.; Giraudon, J. M.; Toupet, L.; Salapala, J.; Guerchais, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 3490−3491.

(8) (a) Luo, L.; Nolan, S. P. *Organometallics* **1994**, *13*, 4781−4786. (b) Luo, L.; Zhu, N.; Zhu, N.-J.; Stevens, E. D.; Nolan, S. P.; Fagan, P. J. *Organometallics* **1994**, *13*, 669−675. (c) Luo, L.; Nolan, S. P.; Fagan, P. J. *Organometallics* **1993**, *12*, 4305−4311. (d) Luo, L.; Nolan, S. P. *Inorg. Chem.* **1993**, *32*, 2410−2415. (e) Luo, L; Nolan, S. P. *Organometallics* **1992**, *11*, 3483−3486.

(9) (a) Nguyen, S. T.; Grubbs, R. H.: Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 9858−9859. (b) Fu, G. C.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 9856−9857. (c) Nguyen, S. T.; Johnson, L. K. Grubbs, R. H.: Ziller, J. W. *J. Am. Chem. Soc.* **1992**, *114*, 3974−3975.

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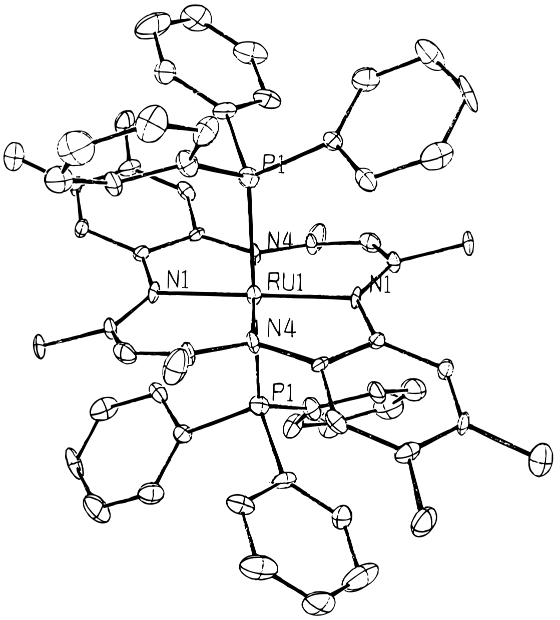

Figure 1. ORTEP of $Ru(omtaa)(PPh_3)_2$ (**1**) with ellipsoids drawn in at 50% probability.

according to eq 4.

$$Cl_2Ru(PPh_3)_3 + Li_2(Me_8taa) \xrightarrow[25\ °C]{CH_2Cl_2} \underset{\mathbf{1}}{(Me_8taa)Ru(PPh_3)_2} + 2LiCl + PPh_3 \quad (4)$$

The NMR spectroscopic data, in view of the simple pattern present in the phenyl region, indicated a very symmetrical structure for **1**. A single crystal diffraction study was carried out on crystals grown from saturated toluene solution of **1** in order to confirm the suspected high symmetry present in this complex.[10] The ruthenium center in $(Me_8taa)Ru(PPh_3)_2$ (**1**) is in an octahedral geometry surrounded by the four nitrogen (as equatorial ligands) of the Me_8taa ligand and two PPh_3 in axial positions. The principal structural feature of **1** is the unusual tetraazannulene ligand geometry. The ligand is found to be in a steplike arrangement. This orientation is similar to the Me_4-taa ligand in $(Me_4taa)Ru(PPh_2Me)_2$.[4b] This geometry represents a distortion of the ligand compared with H_2Me_8taa which adopts a saddle shape geometry.[5] The two PPh_3 ligands are in a mutually trans arrangement separated by 180° (see Tables 1 and 2). The four nitrogen atoms of the tetraazaannulene ligand are coplanar, with one phenyl ligand tipping below the plane defined by the four nitrogens and the other tipping upward, thereby creating the steplike orientation about the equatorial binding positions of Me_8taa. This geometry can be contrasted to a number of porphyrin structures where the equatorial ligand is planar.[11]

The presence of $Ru-PPh_3$ bonds in **1** suggested that simple substitution reactions for the weakly bound PPh_3 ligand might be possible. $(Me_8taa)Ru(PPh_3)_2$ was found to cleanly react with more basic monodentate phosphines and can be used as a synthon for the preparation of other $Ru(Me_8taa)(L)_n$ complexes, as illustrated below.[12,13]

Table 1. Summary of Crystallographic Data for $Ru(Me_8taa)(PPh_3)_2$

empirical formula	$C_{62}H_{60}N_4P_2Ru$
crystal dimens (mm)	0.1 × 0.1× 0.1
space group	$P\bar{1}$
unit cell dimens	
a, Å	11.521(9)
b, Å	13.360(12)
c, Å	16.383(10)
α, deg	80.37(6)
β, deg	83.73(6)
γ, deg	80.77
V, Å^3	2445(5)
Z, molecule/cell	2
density (calcd), g/cm^3	1.391
temp, K	100(2)
X-ray wavelength, Å	0.710 73
diffractometer	Enraf-Nonius CAD4
monochromator	highly ordered graphite crystal
scan type	$\theta - 2\theta$
data collcd	$0 \le h \le 13, -15 \le k \le 15,$ $-19 \le l \le 19$
2θ range, deg	4.0−50.0
abs cor	empirical (ψ-scan method)
no. of reflns measd	8550
no. of obsd reflns ($I > 3\sigma$)	4516
R_F (obsd data), %	6.00
R_{wF}, %	7.29
goodness of fit	2.15
number of params	821
residual density, e/Å^3	
max	+1.07
min	−1.20

$$Ru(Me_8taa)(PPh_3)_2 + 2PEt_3 \xrightarrow{THF} \underset{\mathbf{2}}{Ru(Me_8taa)(PEt_3)_2} + 2PPh_3 \quad (5)$$

$$Ru(Me_8taa)(PPh_3)_2 + dmpm \xrightarrow{THF} \underset{\mathbf{3}}{Ru(Me_8taa)(dmpm)} + 2PPh_3 \quad (6)$$

$$dmpm = Me_2PCH_2PMe_2,\ \text{bis(dimethylphosphinomethane)}$$

At room temperature, the ^{31}P NMR spectrum of **1** displays a singlet at 131.9 ppm (vs 85% H_3PO_4). Variable temperature ^{31}P NMR displays two distinct phosphorus signals indicative of two different phosphorus environments present at low temperature. We took this to indicate the presence of a major and minor isomer. Efforts to isolate the minor component have thus far been unsuccessful. We attribute the geometry of the minor isomer as one where the PPh_3 ligands adopt a cis arrangement. The minor isomer does not appear to be a byproduct of the reaction but is a component of a dynamic isomerization process, according to preliminary variable temperature ^{31}P NMR studies. The existence of such a species (and dynamic process) suggested to us the possibility of catalysis. Complex **1** was tested for both the hydrogenation and isomerization of 1-hexene in tetrahydrofuran and methanol. Prelimi-

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(10) Cell dimensions were determined by least squares refinement of the measured setting angles of 25 reflections with $4° < 2\theta < 50°$. The structure was solved using MULTAN 80 analysis and refined by full-matrix least-squares techniques. Two different molecules are found in the unit cell. These differ by a variation of torsion angles in the triphenylphosphine P−C bond.

(11) See for example: (a) Pacheco, A.; James, B. R.; Rettig, S. J. *Inorg. Chem.* **1995**, *34*, 3477−3484. (b) Ariel, S.; Dolphin, D.; Domazetis, B. R.; James, B. R.; Leung, T. W.; Rettig, S. J.; Trotter, J.; Williams, G. M. *Can. J. Chem.* **1984**, *62*, 755−762.

(12) For **2**: ^1H-NMR (300 MHz, C_6D_6, 25 °C): δ 1.19 (t, 18 H, CH_3- of PEt_3); δ 1.95 (s, 12 H, CH_3- on annulene ring); δ 2.01 (s, 12 H, CH_3- on benzyl groups); δ 2.12 (q, 12 H, $-CH_2-$ of PEt_3); δ 4.20 (s, 2 H, Hγ); δ 6.68 (s, 4 H, H_{Ar}).

(13) For **3**: ^1H-NMR (300 MHz, THF-d_8, 25 °C): δ 1.46 (s, 12 H, CH_3- of dmpm); δ 1.92 (s, 12 H, CH_3- on annulene ring); δ 1.93 (s, 12 H, CH_3- on benzyl groups); δ 1.97 (s, 2 H, $-CH_2-$ of dmpm); δ 4.00 (s, 2 H, Hγ); δ 6.47 (s, 4 H, H_{Ar}).

nary kinetic results, in THF, under 1 atm of hydrogen at 25 °C, displays a turnover frequency of 253 h^{-1} for the hydrogenation of 1-hexene.[14] This compares to a catalytic activity of 118 h^{-1} for Ru(OCOMe)$_2$(PPh$_3$)$_2$ under the same experimental conditions.[15] At 50 °C, a turnover frequency for the isomerization of 1-hexene was found to be 840 h^{-1}, in methanol.[16] Solvent selection appears critical in these studies and further investigations focusing on catalytic mechanistic details involving this and related complexes are ongoing.

Conclusion

The described synthetic approach is one that can lead to gram-quantity isolation of ruthenium tetraazaannulene complexes. The PPh$_3$ adduct is labile toward ligand substitution. Complex **1** shows catalytic activity in the hydrogenation of unsubstituted alkenes as well as in isomerization processes. Preliminary kinetic studies on these catalytic systems show them to be moderately active. From ^{31}P NMR evidence, the catalyst is believed to be the cis-isomer of **1** since mutually cis vacant sites are required to perform the described conversions. Present efforts are directed toward testing the generality of the synthetic approach as it applies to porphyrin and porphyrin-like molecules as well as exploring the catalytic activity of these complexes toward olefins and other substrate transformations.

Table 2. Selected Bond Distances (Å) and Bond Angles(deg) for Ru(Me$_8$taa)(PPh$_3$)$_2$

Bond Lengths[a]			
Ru(1)−P(1)	2.419(3)	Ru(1)−N(1)	2.027(6)
Ru(1)−N(4)	2.033(7)	N(1)−C(2)	1.419(12)
N(1)−C(7)	1.304(10)	N(4)−C(3)	1.369(11)
N(4)−C(5)	1.341(9)	P(1)−C(31)	1.828(10)
P(1)−C(37)	1.842(8)	P(1)−C(43)	1.816(9)
N(11)−C(10)	1.430(11)	N(11)−C(12)	1.317(12)
Bond Angles[a]			
P(1)−Ru(1)−P(1)	180.0	P(1)−Ru(1)−N(1)	89.4(3)
P(1)−Ru(1)−N(1)	90.6(2)	P(1)−Ru(1)−N(4)	89.9(2)
P(1)−Ru(1)−N(4)	90.1(2)	N(1)−Ru(1)−N(1)	180.0
N(1)−Ru(1)−N(4)	99.4(3)	N(1)−Ru(1)−N(4)	80.7(3)
N(1)−Ru(1)−N(4)	80.7(3)	N(1)−Ru(1)−N(4)	99.4(3)
N(4)−Ru(1)−N(4)	180.0	Ru(1)−P(1)−C(43)	115.7(3)
C(31)−P(1)−C(37)	102.3(4)	C(31)−P(1)−C(43)	104.1(4)
C(37)−P(1)−C(43)	100.9(4)		

[a] Numbers in parentheses are the estimated standard deviations.

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Supporting Information Available: Tables of atomic coordinates, selected distances and angles, anisotropic thermal parameters and hydrogen bond distances for **1** (23 pages). Ordering information is given on any current masthead page.

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(14) In a typical catalytic run, 4.5 mL of THF and 3 mg (0.003 mmol) of **1** were charged in a 25 mL flask. Then, under 1 atm of H$_2$, the solution was vigorously stirred and 3 mmol of 1-hexene was syringed into the solution. The hydrogenation rate was followed by measuring the rate of hydrogen uptake. A similar experiment was carried out in the presence of mercury as a radical scavenger with no appreciable change in the rate of hydrogen uptake. After completion, the reaction products were identified by GCMS, which showed total conversion to hexane.

(15) Rose, D.; Gilbert, J. D.; Richardson, R. P.; Wilkinson, G. *J. Chem Soc. A)* **1969**, 2610−2615.

(16) In a typical experiment, 3 mmol of 1-hexene, 3 mg (0.003 mmol) of **1**, and 1 mL of CD$_3$OD were charged in a J-Young NMR tube maintained at 50 °C. ^{1}H NMR spectroscopy was used to measure the isomerization rate following the disappearance of terminal olefinic protons.