^{13}C–H coupling (cf. δ −6.6 ppm, $J(PtH)$ = 779 Hz, and $J(PH)_{trans}$ = 182 Hz in $[Pt(H)(OSO_2CF_3)(dbpp)]$). The IR spectrum (CH_2Cl_2) of **3** shows $\nu(PtH)$ at 2085 cm^{-1}. These observations are consistent with a *cis*-ethene–hydride ground-state structure for **3** (structure A, Scheme II).

Previously we have shown that the extent of $\underline{Pt–H–C}_\beta$ bonding in complexes of the type $[Pt(C_7H_{11})(P\frown P)]^+$ is controlled by the bulk of the phosphine ligand.[7] The results described in this communication show that the ethene–hydride/ethyl system is much more sensitive to the diphosphine ligand and the system can be fine-tuned between the ethene–hydride and agostic ethyl extremes. Brookhart et al.[1b] have suggested that it is electronic factors that determine whether the complex cations $(Rh(\text{“}C_2H_5\text{”})(L)(C_5Me_5)]^+$ are agostic ethyl (L = C_2H_4) or ethene–hydride species (L = PR_3). In the cases **1–3** reported here, the factors involved must be more subtle and must be primarily related to the angle subtended at platinum by the two phosphorus atoms (ca. 90, 100, and 105° for dbpe, dbpp, and dbpx, respectively). Thorn and Hoffmann suggested[8] that the optimum P–Pt–P angle rises from ca. 95° at the start to 110° at the "transition state" (which closely resembles the agostic alkyl structure), during the cis migration of hydride to a coordinated ethene, in the model species $[Pt(H)(C_2H_4)(PH_3)_2]^+$. The evidence we present is also in full accord with other aspects of their theoretical model in showing (i) very fast cis-migration in a d^8 four-coordinate *cis*-alkene–hydride and (ii) a very low barrier to alkene rotation in these species. The control apparently exerted by the P–Pt–P angle on the agostic alkyl vs alkene–hydride isomerism was not anticipated by Thorn and Hoffmann but is implicit in their model and has now been realized experimentally. Finally, the observation that the phosphorus atom environments in **1–3** are *not* averaged in the NMR spectra implies *either* that the methyl group rotation (see Scheme II) occurs without full methyl group dissociation[9] *or* that the 14e $[Pt(\sigma\text{-}C_2H_5)(P\frown P)]^+$ species (C) is T-shaped and not readily transformed (via a Y-shaped intermediate (D)) to an equivalent T-shaped species (C′) with phosphorus sites exchanged. The latter process was considered by Thorn and Hoffmann, and a very low activation energy was assigned. It may be significant that the ^{31}P NMR signals of **1** are broad at room temperature, possibly indicating that the C ↔ C′ process is becoming rapid at this temperature (activation barrier >12.5 kcal mol^{-1}). Thermal instability of **1** at higher temperatures has so far prevented a more detailed NMR study of this process.

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Supplementary Material Available: Tables of atomic coordinates, bond lengths, bond angles, anisotropic displacement parameters, and hydrogen atom parameters for $[Pt(C_2H_5)(dbpp)][CB_{11}H_{12}]$ and further experimental details on the preparation of compounds in Scheme I with spectroscopic data (18 pages); a listing of observed and calculated structure factors for **1** (42 pages). Ordering information is given on any current masthead page.

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Gas-Phase Synthesis of Metallocyclotriynes

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Summary: The interaction of a cyclotriyne ligand with metal ions in the gas phase has been examined by FT-ICR experiments. Complexes of 1:1 and 1:2 (metal to cyclotriyne) ratios have been observed.

We have been examining the reaction chemistry of 12-membered-ring cyclotriynes[1,2] with transition metals. These cyclotriynes are extensively conjugated antiaromatic planar[3] molecules and have cavities that are large enough to fit some low-oxidation-state first-row transition metals. A wide variety of novel metallic complexes of the cyclotriyne TBC (tribenzocyclotriyne, Figure 1) have been synthesized and structurally characterized, including a mononuclear nickel(0) complex,[4] mononuclear and trinuclear copper(I) complexes,[5,6] a cobalt(0) cluster,[7] and a silver(I) sandwich[8] (see Figure 1). The nickel, copper, and cobalt complexes each have a metal in the pocket of the TBC ligand. We have not been able to synthesize complexes of other first-row transition metals with the metal in the pocket. It would be extremely useful to be able to

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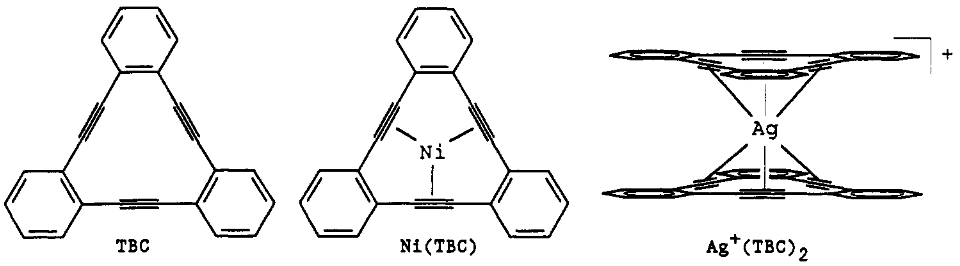

Figure 1.

predict which metals may form sandwich complexes and which metals will fit into the pocket of the cyclotriyne ligands in solution now that a number of new cyclotriyne ligands with different pocket sizes have been synthesized.[9]

In order to make such predictions and to understand gas-phase metal cyclyne chemistry better, we have begun a collaborative effort to study the gas-phase complexation of TBC with transition-metal ions. With use of laser desorption ionization, an ICR ion trap is filled with metal ions M^+, while simultaneously a background pressure of neutral TBC is maintained in the cell by using thermal desorption from the solid probe.[10] The reaction sequence is the two-step process shown in eq 1. Two structures are

$$M^+ \xrightarrow[k_1]{TBC} M^+(TBC) \xrightarrow[k_2]{TBC} M^+(TBC)_2 \qquad (1)$$

likely for the M^+(TBC) complex: one in which the metal fits into the pocket and, for larger M^+, an open-faced sandwich. Considering TBC as a six-electron donor, the electron count around the metal for M^+(TBC) is 6 + *n*, where *n* is the number of valence electrons contributed by the M^+ metal ion. Presumably the $M^+(TBC)_2$ ion is the sandwich compound with the metal ion sandwiched between two TBC ligands. The electron count around the metal for $M^+(TBC)_2$ is 12 + *n*.

The reaction chemistry depicted in eq 1 is unusual with respect to other gas-phase organometallic chemistry[10] because the TBC ligand apparently remains intact in the complex with no neutral leaving group. This result indicates considerable stability for the TBC ligand. Figure 2 shows the reaction rates k_1 and k_2 for the formation of M^+(TBC) and $M^+(TBC)_2$ for the metals studied.[11]

M^+(TBC) is formed with high efficiency for all the transition metals studied; about one collision in two or three results in formation of this product. $M^+(TBC)_2$ is formed with reasonable efficiency (about 10% collisional efficiency) for first-row transition metals through Fe^+ but drops off sharply for Co^+, Ni^+, and Cu^+. Both reactions are efficient for Ag^+, the only second-row transition metal so far studied.

Both of the reactions in eq 1 are association reactions; that is, there is no neutral product to carry off the excess internal energy of the collision complex. Since the pressure was very low (about 5 × 10^{-9} Torr), collisional deactivation of the collision complex is very unlikely, and both of these reactions almost surely proceed by infrared radiative stabilization of the complex to form the association product. As described in detail in a recent analysis,[12] the observed efficiency of infrared radiative complex stabilization allows quite precise estimates of the binding energy of the complex.

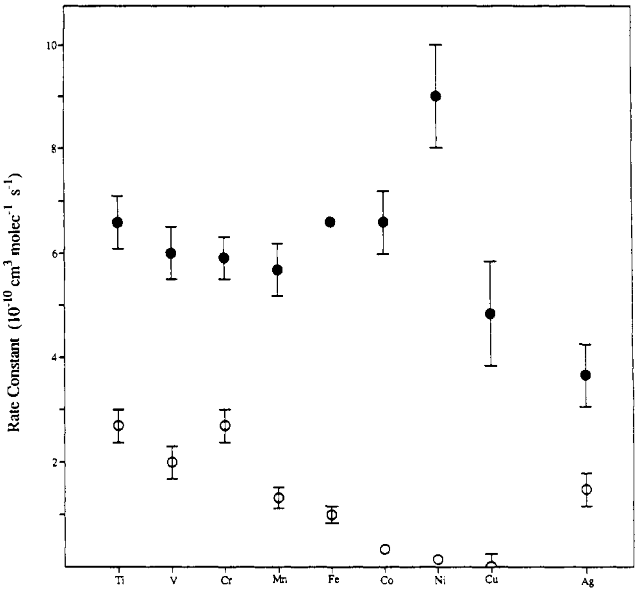

Figure 2. Rate constants for formation of M^+(TBC) (cross-hatched circles) and $M^+(TBC)_2$ (open circles).

The guidelines described in ref 12 indicate that the observed M^+(TBC) complexes are bound by more than 1.3 eV (30 kcal/mol; this is only a lower limit, and the actual value may well be much higher than this). The readily formed $M^+(TBC)_2$ complexes of the early transition metals (as well as $Ag^+(TBC)_2$) must similarly be bound by more than about 1.0 eV (23 kcal/mol), while the inefficiently formed $M^+(TBC)_2$ complex of Cu^+ must be bound by less than 1 eV (on the assumption that it is insufficient binding energy which prevents its stabilization). By this analysis, the $Co^+(TBC)_2$ and $Ni^+(TBC)_2$ complexes can be inferred to have a binding energy near 1.0 eV.

It is not surprising that the M^+–TBC bonding is stronger than 30 kcal/mol. For comparison, Hettich et al.[13] have reported bond strengths of 62 kcal/mol for the V^+–C_6H_6 bond and 55 kcal/mol for the Fe^+–C_6H_6 bond, which may be analogous metal–aromatic cation complexes. M^+–TBC binding energies in the 60 kcal/mol region would be entirely consistent with our estimated lower limits. Since the present discussion gives only lower limits to the binding energies of the metal ion–TBC complexes, a quantitative

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(11) The reaction rate constants were measured relative to k_1 for Fe^+, with the relative uncertainties reflected by the error bars in Figure 2. Since the TBC pressure was unknown, absolute rate constants are not directly available. Conversion of all the rates to absolute rates was carried out by comparison with the rate of protonation of TBC by CH_5^+ and by H_3O^+, which were assumed to transfer protons to TBC at the collision rate. The accuracy of this absolute calibration is unknown but can be hoped to be good within a factor of 2.

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comparison with the metal ion–benzene complexes is not yet possible.

Hettich et al. measured a bond strength of 57 kcal/mol for the $C_6H_6V^+$–C_6H_6 bond.[13] By analogy, the lower limit of 23 kcal/mol on the binding energy of the $M^+(TBC)_2$ complexes of the early-transition-metal ions is not at all surprising. What is striking is the low bond strengths of the $M^+(TBC)_2$ complexes of Cu, Ni, and Co, which are much weaker than any of the organometallic complexes reported by Hettich et al.

It may be suggestive to relate the drop-off in $M^+(TBC)_2$ complex formation, and the apparent associated drop-off in binding energy of the second ligand, to the valence electron count around the metal center. The $Fe^+(TBC)_2$ complex, which appears to lie at the dividing line between efficient and inefficient complex formation, has a 19-electron valence count. The inefficiently formed $M^+(TBC)_2$ complexes of Co^+, Ni^+, and Cu^+ exceed an 18-valence-electron count by two or more. The exception to this trend is $Ag^+(TBC)_2$, which has a formal electron count of 22.[8]

The inefficient formation of $M^+(TBC)_2$ by Co^+, Ni^+, and Cu^+ may stem from size factors rather than electron count. It is possible that the $M^+(TBC)$ complexes of Co^+, Ni^+, and Cu^+ have the metal in the pocket, whereas the other larger first-row M^+ ions and Ag^+ adopt an open-face sandwich structure. A metal encapsulated in the TBC ligand would be less likely to bind another large ligand such as TBC.

The ICR technique provides no direct structural information about the complexes. However, the ready formation and substantial bonding energy of the $M^+(TBC)$ complexes of Co^+, Ni^+, and Cu^+ and the ready formation of the $Ag^+(TBC)_2$ complex are features of the present results which are consistent with what we have observed in solution and the solid state. This is encouraging to the idea that gas-phase results may have predictive value for the formation of mononuclear compounds with other metal systems in the condensed phase.

It will be interesting to observe both the radiative association reactions of metallocyclyne ions with other ligands, as in

$$M^+(TBC) + L \rightarrow M^+(TBC)L$$

and also possible ligand displacement reactions such as

$$M^+(TBC)_2 + L \rightarrow M^+(TBC)L + TBC$$

which should clarify further the binding patterns and bond strengths of gas-phase metallocyclyne complexes and their interactions with small molecules of interest in catalytic chemistry, such as CO, CO_2, CH_4, and CH_3OH.

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Homogeneous Catalytic Hydrogenation. 5. Regioselective Reductions of Mono- and Polynuclear Heteroaromatic Model Coal Compounds Using the (η^5-Pentamethylcyclopentadienyl)rhodium Tris(acetonitrile) Dication as the Catalyst Precursor[1]

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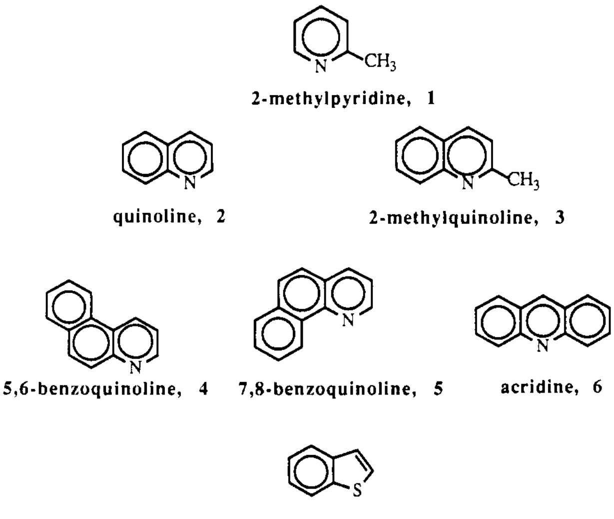
Summary: The regioselective hydrogenation of representative mono- and polynuclear heteroaromatic nitrogen and sulfur model coal compounds such as 2-methylpyridine (**1**), quinoline (**2**), 2-methylquinoline (**3**), 5,6- and 7,8-benzoquinolines (**4** and **5**), acridine (**6**), and benzothiophene (**7**) was studied with the dicationic complex (η^5-pentamethylcyclopentadienyl)rhodium tris(acetonitrile) ($Cp^*Rh(CH_3CN)_3{}^{2+}$) as the catalyst precursor. The order of relative rates as a function of structure was found to be **5** >>> **6** > **2** > **4** > **3** > **7** >> **1**. Replacement of H_2 with D_2 provided information on several of the mechanistic aspects of these selective hydrogenation reactions with compounds **2** and **7** as examples.

Several years ago, we discovered that a variety of rhodium and ruthenium complexes were catalysts for the regioselective hydrogenation of polynuclear heteroaromatic nitrogen model coal compounds, this being the first step in the highly important hydrodenitrogenation reaction.[1]

Chart I


2-methylpyridine, 1
quinoline, 2
2-methylquinoline, 3
5,6-benzoquinoline, 4
7,8-benzoquinoline, 5
acridine, 6
benzothiophene, 7

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