When 1 was allowed to react with PPh_3 in C_6D_6/40% aqueous $NaOD/[PhCH_2NEt_3]^+Cl^-$, no deuterium was incorporated in the product 2; hence, the source of the *o*-phenylene ligand is triphenylphosphine, not the organic phase.

Dehydrochlorination of 1 also occurs in the absence of PPh_3; in this case, however, a complicated mixture results and the ^1H NMR spectrum of the organic phase showed more than 10 different resonances in the hydride region. The intensities of some of these resonances either decreased significantly or disappeared altogether when the reaction was carried out in C_6D_6/60% aqueous $KOH/[PhCH_2NEt_3]^+Cl^-$. This observation indicates that a coordinatively unsaturated, reactive iridium species, formed by the reductive elimination of HCl from 1, reacts with benzene by activating its C–H (C–D) bonds and forming a number of hydrido (deuterido) complexes. It is, then, feasible that the same reactive species is responsible for the formation of 2 when PPh_3 is present in the reaction mixture. Note that the cleavage of P–C bonds in tertiary phosphines by transition-metal complexes often indicates the presence of a coordinatively unsaturated and reactive species.[8] Nonetheless, the mechanism of formation of 2 might be much more complicated than the one suggested above and might involve initial coordination of PPh_3 or OH^- to 1 and cleavage of an Ir–H bond before the elimination of HCl.

The structure of 2 was determined by a single-crystal X-ray diffraction study[9] (Figure 1). Recently, Bergman and co-workers[10] synthesized and completely characterized very similar complexes, $[Ir_2(C_5Me_5)_2(\mu\text{-}OH)(\mu\text{-}PAr_2)(\mu\text{-}C_6H_3R)]$, where Ar = C_6H_5, $p\text{-}CH_3C_6H_4$ and R = H, CH_3. The molecule 2 occupies a special position on the mirror plane normal to the Ir–Ir′ bond, passing through the phosphorus and hydride atoms. The planes of the bridging ligands in 2, namely Ir–H–Ir′ (A), Ir–P–Ir′ (B), and Ir–C(1)–C(1′)–Ir′ (C), form the pairwise different dihedral angles 156.8 (A/B), 91.4 (B/C), and 111.8° (A/C). The Ir–Ir′ bond (2.8901 (4) Å) is substantially elongated in comparison to that found earlier in the $[Ir_2(C_5H_5)_2(CO)_2(\mu\text{-}C_6H_4)]$ complex (2.717 Å);[11] this is evidently due to the influence of the μ_2-hydride ligand. The Ir···Ir separation in Bergman's related complex $[Ir_2(C_5Me_5)_2(\mu\text{-}OH)(\mu\text{-}PPh_2)(\mu\text{-}C_6H_4)]$ was found to be 3.369 (1) Å.[10] Therefore, the replacement of μ-H for μ-OH in 2 leads to deep structural changes. The geometry of the aromatic nucleus of the phenylene group does not exhibit any noticeable distortions, and its mean plane in fact coincides with the C plane, the corresponding dihedral angle being equal to 1.1°. The Cp* rings, which are planar within 0.01 Å, form a dihedral angle of 129.3°.

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Supplementary Material Available: Full details of the structure solution and tables of atomic coordinates, bond lengths and angles, and thermal parameters (4 pages); a listing of structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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[9] Crystal data for **2**: $C_{38}H_{45}Ir_2P$, orthorhombic, space group *Pnam*; at +20 °C a = 18.703 (2) Å, b = 11.143 (1) Å, c = 16.247 (1) Å, D_c = 1.799 g/cm^3, and Z = 4; R = 0.032, R_w = 0.036 for 1793 reflections (λ(Mo Kα), graphite monochromator, $\theta/2\theta$ scan); μ = 78.9 cm^{-1}; DIFABS (minimum absorption correction 0.894; maximum absorption correction 1.431; average absorption correction 0.993). All H atoms, including the bridging hydride atom, were located in the difference Fourier synthesis. The position of the hydride ligand was refined isotropically, whereas the remaining hydrogen atoms were included as fixed contributions with B_{iso} = 5.5 Å^2.

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Control of Intramolecular β-Hydrogen Migration in Coordinatively Unsaturated (Diphosphine)platinum Ethyl Cations

Laura Mole and John L. Spencer*
Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, U.K.

Nicholas Carr and A. Guy Orpen*
Department of Inorganic Chemistry, University of Bristol, Bristol BS8 1TS, U.K.

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Summary: Protonation of the complex $[Pt(C_2H_5)_2(\overset{\frown}{P\ P})]$ or $[Pt(\eta^2\text{-}C_2H_4)(\overset{\frown}{P\ P})]$ ($\overset{\frown}{P\ P}$ = $Bu^t{}_2P(CH_2)_nPBu^t{}_2$ (n = 2, 3) and $o\text{-}(Bu^t{}_2PCH_2)_2C_6H_4$) affords a series of cations characterized as either ethene–hydride or agostic ethyl complexes $[Pt(H)(\eta^2\text{-}C_2H_4)(\overset{\frown}{P\ P})]^+$ or $[Pt(C_2H_5)(\overset{\frown}{P\ P})]^+$ by NMR spectroscopy and, in the case of $[Pt(C_2H_5)\{Bu^t{}_2P(CH_2)_3PBu^t{}_2\}][CB_{11}H_{12}]$, by single-crystal X-ray diffraction. The size of the chelating diphosphine ligand is shown to control the extent of transfer of a hydrogen atom from the β-carbon of the coordinated ethyl group to platinum with the smaller diphosphines favoring transfer to the metal. All the complexes show remarkably low barriers to intramolecular rearrangement.

Complexes with three-center, two-electron M–H–C_β (β-agostic) interactions in their ground states can be viewed as models for intermediates along the migratory insertion/β-elimination pathway.[1] The energy difference between alkene-hydride and alkyl forms is often small, and consequently, some closely related complexes adopt different structures. For example, replacing an ethene by a phosphine ligand in species $[Rh(\text{“}C_2H_5\text{”})(L)(C_5Me_5)]^+$ alters the preferred geometry[1b] from $[Rh(C_2H_5)(C_2H_4)(C_5Me_5)]^+$ to $[Rh(H)(C_2H_4)(PR_3)(C_5Me_5)]^+$.

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[1] (a) Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1 and references therein. (b) Brookhart, M.; Lincoln, D. M.; Bennett, M. A.; Pelling, S. *J. Am. Chem. Soc.* **1990**, *112*, 2691.

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Table I. Selected ^{13}C NMR Data for the Complexes $[Pt(``^{13}C_2H_5")(P\frown P)][BF_4]$ (1–3)[a]

A. Spectra at 298 K

complex	$\delta(C)$	$J(PtC)$	$J(PC)$	$J(CH)$
1	16.1	91	18	67
2	15.2	95	18	67
3	48.2	55	13	65

B. Spectra at Low Temperature

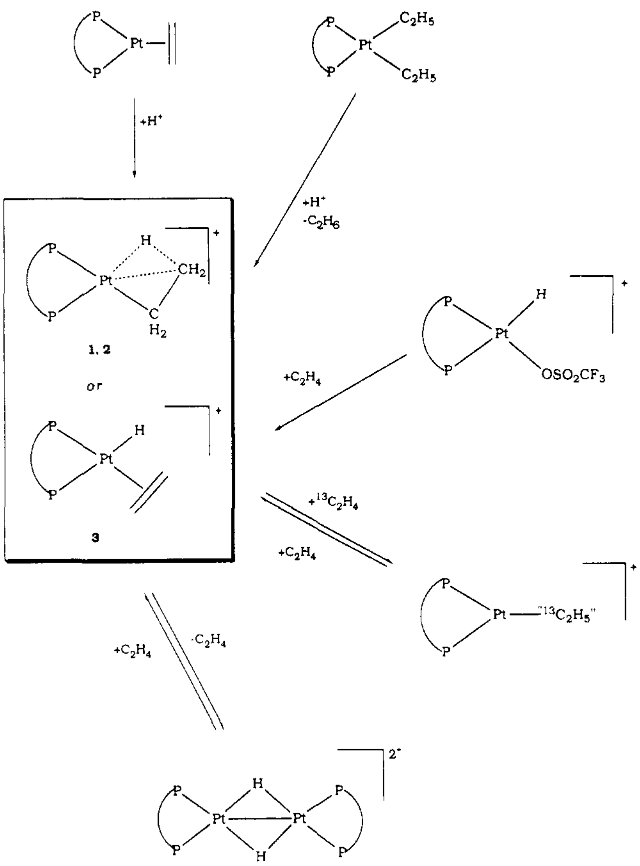
complex	temp, K	$\delta(C_\alpha)$	$J(C_\alpha H)$	$J(C_\alpha C_\beta)$	$J(PC_\alpha)$	$J(PtC_\alpha)$	$\delta(C_\beta)$	$J(C_\beta H_{ag})$	$J(C_\beta H_t)$
1	145	22.0	155	29	39	218	9.0	75	155
2	145	22.0	158	26	41	200	8.2	60	153
3	180	51.5	160	...	*b*	*b*	*c*		

[a] Resonances are given for the ethyl moiety only; spectra were determined for samples in CD_2Cl_2 or CD_2Cl_2/Me_2O solution with δ values in ppm and J values in Hz. [b] Not observed. [c] One signal for both carbon nuclei.

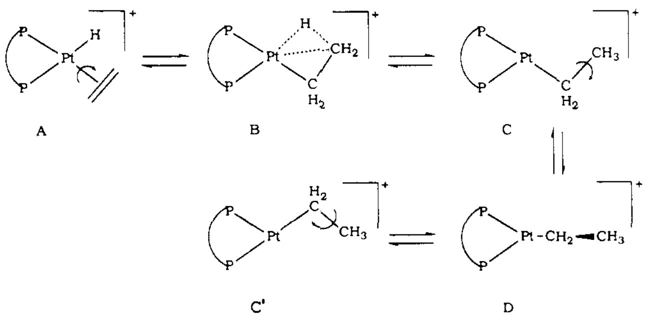
The change from Co(III) to Fe(II) also causes a structural rearrangement, e.g. from $[Co(C_2H_5)(PMe_3)(C_5Me_5)]^+$ to $[FeH(C_2H_4)(PMe_3)(C_5Me_5)]$.[2,3] In this communication we report a new series of (diphosphine)Pt^{II} cations in which changes in the ancillary diphosphine ligands control the balance between the agostic ethyl and ethene–hydride forms. Understanding and controlling this balance may be critical in chemistry such as that of alkene oligo- or polymerization reactions since the alkene–hydride species is an important intermediate in chain termination, whereas the agostic alkyl species is a suitable precursor for further chain growth.[4] It should be borne in mind, however, that ground-state structure often provides only indirect clues to reactivity.

We have developed five routes of varying generality to species of the type $[Pt(``alkyl")(P\frown P)]^+$, as outlined in Scheme I. In order to elucidate the structures of these cations by means of $^{13}C$ NMR spectroscopy, the synthesis of a series of doubly $^{13}C$ labeled complexes $[Pt(``^{13}C_2H_5")(P\frown P)][BF_4]$ (1–3; $P\frown P$ = o-$(Bu^t{}_2PCH_2)_2C_6H_4$ (dbpx) (1), $Bu^t{}_2P(CH_2)_3PBu^t{}_2$ (dbpp) (2), and $Bu^t{}_2P(CH_2)_2PBu^t{}_2$ (dbpe) (3)) was undertaken.[5] Complexes 1 and 2 were prepared by ethene exchange between unlabeled 1 or 2 and $^{13}C_2H_4$ in an NMR tube. However, for 3 this exchange process is relatively slow and 3 was therefore synthesized by protonation of $[Pt(\eta^2\text{-}^{13}C_2H_4)(dbpe)]$.

Scheme I



Scheme II



For all the complexes (1–3), facile scrambling of the C_2H_5 moiety results in the equivalence of all five protons and

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(5) For example, the compound $[Pt(C_2H_5)_2(Bu^t{}_2P(CH_2)_3PBu^t{}_2)]$ was prepared by heating an equimolar amount of $[Pt(C_8H_{12})(C_2H_5)_2]$ (0.614 g, 1.69 mmol) and $Bu^t{}_2P(CH_2)_3PBu^t{}_2$ (0.565 g, 1.69 mmol) in toluene solution (5 cm^3) under N_2 at 368 k for 20 h. After the mixture was cooled to ambient temperature, the solvent was reduced to ca. 2 cm^3 in vacuo. Further cooling to 248 K afforded $[Pt(C_2H_5)_2(Bu^t{}_2P(CH_2)_3PBu^t{}_2)]$ as clear, beige crystals (0.843 g, 1.44 mmol) in 85% yield. ^1H NMR (C_6D_6): δ 1.45 (q, 4 H, $J(HH)$ = 7 Hz, $J(PtH)$ = 72 Hz, CH_2CH_3), 1.25 (d, 36 H, $J(PH)$ = 11 Hz, Bu^t), 2.05 ppm (m, 6 H, PCH_2). The methyl signal is obscured by the Bu^t signals. ^{13}C NMR (C_6D_6): δ 11.1 (dd, $J(PC)$ = 10 and 97 Hz, $J(PtC)$ = 692 Hz, CH_2CH_3), 17.2 (s, $J(PtC)$ = 23 Hz, CH_2CH_3), 22.1 (t, $J(PC)$ = 9 Hz, PCH_2CH_2), 25.2 (m, PCH_2), 31.2 (s, $C(CH_3)_3$), 37.0 ppm (m, $C(CH_3)_3$). ^{31}P NMR (C_6D_6): δ 18.3 ppm, $J(PtP)$ = 1634 Hz. Anal. Calcd for $C_{23}H_{52}P_2Pt$: C, 47.18; H, 8.95. Found: C, 46.86; H, 9.02. A solution of $[Pt(C_2H_5)_2(Bu^t{}_2P(CH_2)_3PBu^t{}_2)]$ in diethyl ether at 0 °C was treated with an equimolar amount of $HBF_4 \cdot OMe_2$, upon which a cream-colored solid precipitated. The supernatant liquid was decanted and the precipitate washed with diethyl ether and then dried in vacuo to afford $[Pt(C_2H_5)(Bu^t{}_2P(CH_2)_3PBu^t{}_2)][BF_4]$ in ca. 80% yield. The sample of $[Pt(^{13}C_2H_5)(dbpp)]^+$ was prepared in situ in an NMR tube: into a frozen and degassed solution of $[Pt(C_2H_5)(dbpp)]^+$ in ca. 0.4 cm^3 of CD_2Cl_2 at 77 K was condensed a 10% molar excess of $^{13}C_2H_4$, followed by Me_2O. The tube was sealed and warmed to 293 K for 0.5 h to allow the exchange reaction to take place. ^1H NMR (CD_2Cl_2; $^{12}C_2$ sample): δ 0.77 (d, 5 H, $J(PH)$ = 13 Hz, $J(PtH)$ = 65 Hz), 1.27 (d, 18 H, $J(PH)$ = 14 Hz, Bu^t), 1.32 (d, 18 H, $J(PH)$ = 14 Hz, Bu^t), 2.2 ppm (m, 6 H, PCH_2, CH_2). ^{13}C NMR (CD_2Cl_2): δ 15.9 (sx of d, $^1J(CH)_{av}$ = 67 Hz, $J(PtC)$ = 95 Hz, $J(PC)$ = 18 Hz, C_α and C_β), 18.5 (d, $J(PC)$ = 11 Hz, PCH_2), 19.1 (dd, $J(PC)$ = 7 and 31 Hz, PCH_2), 24.5 (s, $J(PtC)$ = 59 Hz, PCH_2CH_2), 29.9 (d, $J(PC)$ = 4 Hz, $C(CH_3)_3$), 30.3 (d, $J(PC)$ = 2 Hz, $C(CH_3)_3$), 36.4 (d, $J(PC)$ = 23 Hz, $J(PtC)$ = 15 Hz, $C(CH_3)_3$), 38.4 ppm (d, $J(PC)$ = 29 Hz, $J(PtC)$ = 61 Hz, $C(CH_3)_3$). ^{31}P NMR (CD_2Cl_2): δ 47.9 ($J(PtP)$ = 4919 Hz), 37.6 ppm ($J(PtP)$ = 2703 Hz). Anal. Calcd for $C_{21}H_{47}BF_4P_2Pt$: C, 39.21; H, 7.36. Found: C, 38.77; H, 7.38.

Table II. Selected ^{1}H and ^{31}P NMR Data for the Complexes [Pt("C_2H_5")($P\frown P$)][BF_4] (1-3)[a]

A. Spectra at 298 K

complex	$\delta(P_1)$[b]	$J(PtP_1)$	$\delta(P_2)$	$J(PtP_2)$	δ(H)	J(PtH)	J(PH)
1	38.0	2800	53.2	5220	0.7		12
2	38.1	2707	48.4	4919	0.8	65	13
3	104.8	2965	90.6	2980	1.7	63	22

B. Spectra at Low Temperature

complex	temp, K	$\delta(P_1)$	$J(PtP_1)$	$\delta(P_2)$	$J(PtP_2)$	δ(H)	J(PtH)	J(PH)
1	203	34.5	2778	50.0	5123	-2.8[c]		
2	186	36.8	2680	47.4	4923	-2.6[c]		
3	186	106.3	2971	91.5	2645	-4.6[d]	508	109

[a] Spectra were determined for samples in CD_2Cl_2 solution with δ values in ppm and J values in Hz. [b] P_1 is cis to the hydridic hydrogen and P_2 is trans to the hydridic hydrogen. [c] Recorded at 165 K. [d] Recorded at 180 K.

both carbon atoms (but *not* the phosphorus atoms) such that sharp averaged signals are observed in NMR spectra above 240 K. For example, a single resonance (intensity 5 H) at δ 0.8 ppm, strongly coupled to only one phosphorus nucleus, is observed in the ^{1}H NMR spectrum of 2 at 298 K. These observations are consistent with rapid intramolecular rearrangement processes involving both the ethene–hydride form, in which ethene rotation is facile, and the alkyl form, for which methyl group rotation is rapid (Scheme II). The free energy of activation for these processes may be estimated (for 2 $\Delta G^{\ddagger}$ = ca. 8 ± 1.5 kcal mol^{-1} for a coalescence temperature of 190 K) and serves as an upper bound[1b] on the energy difference beteen the agostic ethyl and ethene–hydride forms.

Parameters derived from ^{13}C NMR spectroscopy, particularly ^1J(CH), have proved useful in characterizing agostic interactions.[1] At 298 K the ^{13}C NMR signals ascribed to the C_2 moiety appear as binomial sextets with comparable mean values of ^1J(CH) for each of 1–3. However, there are significant differences between the chemical shift and J(PtC) parameters for 3 compared with those of 1 and 2 (Table I). The limiting ^{13}C NMR spectra (145 K) of 1 and 2 are consistent with the presence of ethyl ligands bound to platinum through σ-alkyl and β-agostic C–H–M bonds. Thus, in 2 C_α resonates at δ 22.0 ppm (t, ^1J(CH) = 158 Hz) whereas C_β at 8.2 ppm shows triplet and doublet proton coupling (^1J(CH) = 153 and 60 Hz, respectively). The smaller value of ^1J(CH) is typical of complexes with a β-agostic bond.[1] On this basis 2 is assigned an agostic ethyl structure illustrated as B in Scheme II.

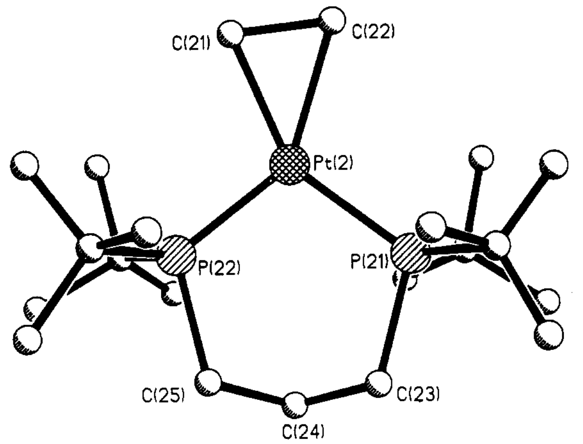

Figure 1. Structure of the cation [Pt(C_2H_5)(dbpp)]$^+$. All hydrogen atoms have been omitted for clarity. Important molecular dimensions include the following (bond lengths in angstroms and angles in degrees): Pt(2)–P(21) = 2.257 (6), Pt(2)–P(22) = 2.194 (6), Pt(2)–C(21) = 2.09 (3), Pt(2)–C(22) = 2.28 (2), C(21)–C(22) = 1.56 (4); P(21)–Pt(2)–P(22) = 104.8 (2), P(22)–Pt(2)–C(21) = 103.7 (7), P(22)–Pt(2)–C(22) = 144.9 (6), P(21)–Pt(2)–C(21) = 151.3 (7), P(21)–Pt(2)–C(22) = 109.7 (6), C(21)–Pt–C(22) = 41.6 (9), Pt(2)–C(21)–C(22) = 75 (1), Pt(2)–C(22)–C(21) = 62 (1).

The NMR evidence was borne out by a low-temperature X-ray crystallographic study on [Pt(C_2H_5)(dbpp)][$CB_{11}H_{12}$][6] (Figure 1). The solid-state structure of the cation, although disordered,[6] is consistent with the NMR spectra of 2 recorded at 145 K, in having the ethyl moiety bound asymmetrically to the platinum center. As compared to an η^2-bound C_2H_4 ligand, the C_α atom is tilted toward the metal (Pt(2)–C(21) = 2.09 (3) Å) and is more nearly trans to a phosphorus atom (P(21)) than is C_β (Pt(2)–C(22) = 2.28 (2) Å), which is tilted away so that the agostic hydrogen may be inferred to occupy the position trans to the second phosphorus atom (P(22)). The agostic hydrogen could not be located. The bond length Pt(2)–P(21) (2.257 (6) Å) trans to C_α is longer than that trans to the agostic bond (Pt(2)–P(22) = 2.194 (6) Å) as expected from the ^{31}P NMR data, where $^1J(PtP_{trans}) \gg {}^1J(PtP_{cis})$ (Table II).

Inspection of the NMR data (Tables I and II) suggests that the ground-state structure of 3 is very different from those of 1 and 2. In contrast to the dramatic differences observed in the values of ^1J(PtP) for phosphorus nuclei cis and trans to the agostic bond in 1 and 2, the values of ^1J(PtP) for 3 are almost identical at 298 K. Furthermore, one of the coupling constants shows a marked temperature dependence consistent with the presence of an equilibrium between agostic ethyl and ethene hydride forms of 3 in which the ethene hydride is the dominant species. In the ^{13}C NMR spectrum at 180 K the C_2 moiety gives rise to a single multiplet with a gross triplet structure due to proton coupling (^1J(CH) ≈ 160 Hz; cf. 130 Hz for coordinated C_2H_4 in [Pt(η^2-C_2H_4)(dbpe)] and 157 Hz in free C_2H_4). The ^{1}H NMR spectrum of 3 recorded at 180 K shows a signal at high field typical of a hydride (δ -4.6 ppm, J(PtH) = 508 Hz, $J(PH)_{trans}$ = 109 Hz) with no measurable

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[6] This salt was prepared by the reaction of [Pt(C_2H_5)$_2$(dbpp)] with the carbaborane acid *closo*-$CB_{11}H_{13}$; and the complex cation was shown to be identical with that of 2 by NMR spectroscopy; all other salts gave solids of poorer diffraction quality. Crystals of [Pt(C_2H_5)(dbpp)][$CB_{11}H_{12}$] were grown by the vapor diffusion of OEt_2 into a CH_2Cl_2 solution of the compound. Crystal data: $C_{22}H_{59}B_{11}P_2Pt$, M_r = 699.7, monoclinic, space group $P2_1/c$ (No. 14), a = 17.715 (3) Å, b = 22.576 (4) Å, c = 16.466 (3) Å, β = 90.046 (13)°, V = 6584 (2) Å^3, Z = 8, D_x = 1.411 g cm^{-3}, $\bar{\lambda}$ = 0.71069 Å, μ(Mo Kα) = 44.1 cm^{-1}, F(000) = 2832, T = 190 K. R = 0.048, R_w = 0.056 and S = 1.47 for 6241 reflections with $I > 2\sigma(I)$. Both independent cations in the asymmetric unit are subject to a partial 2-fold site disorder about a psuedo center of inversion near the geometric center of the cation, with PBu^t_2 groups common to both orientations; occupancy factors of 0.802 (4) and 0.859 (4) were refined for the major orientation in each site. The structures of the two cations are similar, and therefore, the molecular parameters quoted and the illustration in Figure 1 refer to the major orientation of the better ordered of the two. Although the final goodness of fit (S) and the agreement between independent molecules are satisfactory, since the disorder affects the entire cation, and in particular the metal and ethyl atomic sites, care should be taken not to overinterpret the bond lengths and angles reported.

^{13}C-H coupling (cf. δ -6.6 ppm, J(PtH) = 779 Hz, and $J(\mathrm{PH})_{\mathrm{trans}}$ = 182 Hz in [Pt(H)(OSO$_2$CF$_3$)(dbpp)]). The IR spectrum (CH$_2$Cl$_2$) of **3** shows ν(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 Pt-H-C$_\beta$ bonding in complexes of the type [Pt(C$_7$H$_{11}$)($\mathrm{P}^\frown\mathrm{P}$)]$^+$ 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("C$_2$H$_5$")(L)(C$_5$Me$_5$)]$^+$ are agostic ethyl (L = C$_2$H$_4$) 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$_2$H$_4$)(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(σ-C$_2$H$_5$)($\mathrm{P}^\frown\mathrm{P}$)]$^+$ 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 $\leftrightarrow$ 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.

Acknowledgment. This work was supported by the Science and Engineering Research Council.

Supplementary Material Available: Tables of atomic coordinates, bond lengths, bond angles, anisotropic displacement parameters, and hydrogen atom parameters for [Pt(C$_2$H$_5$)(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

Robert C. Dunbar,[*] Don Solooki, Claire A. Tessier,[†] and Wiley J. Youngs[*,†]

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

Bruce Asamoto

BP America Research & Development, 4440 Warrensville Road, Cleveland, Ohio 44128-2387

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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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[†] Present address: Department of Chemistry, The University of Akron, Akron, OH 44325-3601.

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