onstrates that the chemical reaction following the initial electron transfer (C in the EC mechanism) is first order in the reactant 1. It is a further confirmation that dimerization or another coupling reaction (eq 5) follows the rapid loss of NCMe (eq 4).

Conclusions

1. Detailed voltammetry studies have demonstrated that the title compound undergoes a one-electron reduction, irreversible up to scan rates of 20 V/s at ca. -1.4 V versus SCE.

2. 1 accepts an electron rapidly from a Pt electrode (eq 3) and then undergoes loss of NCMe (eq 4) in less than 50 ms at ambient temperatures, producing a 17-electron radical.

3. The radical produced in eq 4 couples rapidly to give in excess of 60% of the metallacyclononatetraene complex

2, in which linking of the four alkynes has occurred.

4. The 17-electron radical also forms a secondary product which may be the metal-metal bonded dimer $[CpMo(C_2Me_2)_2]_2$ (3).

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Supplementary Material Available: NMR and mass spectra of mixture of 2 and the secondary reaction product and a table of chemical shifts of K reduction and bulk electrolysis products in acetone- d_4 (4 pages). Ordering information is given on any current masthead page.

Synthesis and Reactivity of Benzyne Derivatives of Rhenium Formed by Facile Ortho-Hydrogen Abstraction in a Homoleptic Rhenium Aryl. X-ray Structure of the Cationic Benzyne $[Re(\eta^2-2-MeC_6H_3)(2-MeC_6H_4)_2(PMe_3)_2][I_5]$

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The paramagnetic benzyne complexes $\operatorname{Re}(\eta^2-2\cdot\operatorname{MeC}_6H_3)(2\cdot\operatorname{MeC}_6H_4)_2(\operatorname{PMe}_2R)_2$ (R = Me, 2a; R = Ph, 2b) are formed at low temperature via ligand-induced ortho-hydrogen abstraction on addition of phosphine to the homoleptic aryl $\operatorname{Re}(2\cdot\operatorname{MeC}_6H_4)_4$ (1). Complexes 2 are oxidized under mild conditions to the benzyne cations [2][X] (X = PF_6^-, BPh_4^-, OTf^-, Co(CO)_4^-, I_5^-) with $E_{1/2} = -0.90$ V (relative to Cp_2Fe at 0.00 V). The cations are reduced by strong nucleophiles, e.g., LiBEt₃H, Me₃SiCH₂MgCl, in THF, back to the neutral species. NMR data for [2][X] are in agreement with the solid-state structure, determined for [2a][I_5] by X-ray crystallography. Crystals are orthorhombic, space group $Pna2_1$, with a = 18.735 (2), b = 13.954 (5), c = 14.193 (2) Å, Z = 4, $D_{calcd} = 2.23$ g cm⁻³. The geometry of the cation can be described as distorted trigonal bipyramidal with the benzyne symmetrically η^2 -bound at an equatorial site (Re-C(benzyne) = 2.02 (2) Å) and with axial phosphines (Re-P = 2.421 (5) and 2.435 (5) Å); the equatorial Re-C(2-MeC_6H_4) distances are 2.09 (1) Å.

Interest in the chemistry of transition-metal-benzyne derivatives has increased since the first example of such a compound was structurally characterized in 1979.¹ Stable mononuclear benzyne derivatives are now known for Zr,² Nb,^{1,3} Ta,^{1,3} and Ni;⁴ in addition, the intermediacy of such species has been postulated in a number of instances.⁵ In all cases except Ni, benzyne formation evidently proceeds via ortho-hydrogen abstraction from a high-valent, electrophillic, d⁰ metal complex, often requiring prolonged thermolysis at high temperature. The reactivity of metal-benzyne bonds has been investigated in a few cases.^{1,2,4} Insertion of alkenes, alkynes, and nitriles,

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for instance, appears to be facile; metal-benzyne bonds have been cleaved quite readily by reagents such as MeOH, MeI, and I₂.

In the course of studies on the chemistry of homoleptic aryl compounds, we have discovered a new, remarkably mild synthetic route to the first examples of rhenium benzyne derivatives, starting from the paramagnetic, 11electron rhenium(IV) (d³) tetraaryl, Re(2-MeC₆H₄)₄⁶ (1). A preliminary account has appeared.⁷

Results and Discussion

Preparation and Properties of Re $(\eta^2-2\cdot MeC_6H_3)$ (2-MeC₆H₄)₂(PMe₂R)₂. Addition of phosphine (PMe₃ or PMe₂Ph, ≥ 2 equiv.) to toluene or THF solutions of 1 at -80 °C results in a color change from dark red-black to deep purple. On warming, the color gradually changes (at ca. -40 °C with PMe₃; -15 °C with PMe₂Ph) to yield a deep maroon-red solution. Benzyne complexes Re(η^2 -2-MeC₆H₃)(2-MeC₆H₄)₂(PMe₂R)₂ (**2a**, R = Me; **2b**, R = Ph) were isolated in high yields after removal of volatiles and crystallization from hexane (eq 1). The purple interme-



diate is not observed if the reaction is conducted at room temperature. Toluene liberated was detected by MS analysis of the volatiles from the reaction in THF; no C_7H_6D was produced when the reaction was repeated in benzene- d_6 . With only 1 equiv of phosphine, warming and workup of the purple solution led to roughly equal amounts of 1 and 2 (separated by fractional crystallization). No reaction was observed between 1 and P-i-Pr₃ from -80 to 20 °C. In refluxing toluene a dark brown mixture was obtained from which no pure product could be isolated. The tetraaryl 1 was completely unreactive toward the bulkier phosphines PMePh₂, PPh₃, PCy₃, and P(SiMe₃)₃; reaction with dmpe in hexane gave an amorphous orange material that was insoluble in common organic solvents. Pyridine and NMe₃ did not react with 1; CO and *t*-BuNC reacted rapidly, but the complex mixtures of products have not vet been identified.

Benzyne derivatives 2 are highly crystalline air-stable materials soluble in hydrocarbon, ethereal, and chlorinated solvents. Parent ions are observed in the mass spectrum together with ions due to loss of one and then both phosphines. They are paramagnetic with magnetic moments in accord with a single unpaired electron and exhibit



Figure 1. Cyclic voltammogram of 2a in THF 0.2 M $[n-Bu_4N][PF_6]$ at 50 mV s⁻¹, referenced to Cp₂Fe at 0.00 V.



six-line ESR spectra due to coupling of the electron with Re (¹⁸⁷Re, 63%, $I = \frac{5}{2}$; ¹⁸⁵Re, 37%, $I = \frac{5}{2}$). The IR spectrum shows a single C=C stretch (2a, 1568 cm⁻¹; 2b, 1566 cm⁻¹. cf. 1, 1566 cm⁻¹). The X-ray structure of 2b has been reported.⁷

A plausible mechanism is illustrated in Scheme I. A probable first step is nucleophilic attack on 1 by phosphine to form the adduct A. The purple intermediate we observe at -80 °C may correspond to such a species, but hard evidence is currently lacking. Thermally unstable A then rearranges via ortho-hydrogen transfer to liberate toluene and complex B. (Note that 1 is very stable thermally—it melts without decomposition at 140 °C and gives a moderately intense parent ion in the mass spectrum.⁶) Finally, B is trapped by a second equivalent of phosphine to give the isolated product 2. Since both 1 and 2 are isolated when only 1 equiv. of phosphine is used, formation of the initial adduct A must be reversible. Attempts to stabilize B using bulky phosphines [P-i-Pr₃, PCy₃, PPh₃, P(SiMe₃)₃] were unsuccessful-presumably these ligands are too large to form the initial adduct A.

The mechanism of the ortho-hydrogen transfer step is unknown, although several pathways can be considered. A free-radical process is unlikely since no hydrogen abstraction from the solvent was observed; a radical cage mechanism is still possible, however. An unstable species such as A could undergo oxidative addition of an ortho C-H bond to form a benzyne hydride. Reductive elimination of toluene followed by trapping by phosphine would then give the observed product. To test whether any intermediates in the reaction in eq 1 were prone to intermolecular oxidative addition, experiments were repeated in the presence of excess MeI and H₂. However, in neither case was the course of the reaction diverted. A further mechanistic possibility is a simple ortho-hydrogen ab-

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straction via a four-center transition state (Scheme II). Related abstraction processes are common in d⁰ systems.⁸ Note that in the analogous osmium system, $Os(2-MeC_6H_4)_4$ undergoes reductive elimination of biaryl on treatment with Lewis bases.^{7,9}

Redox Chemistry of 2. Results of cyclic voltammetry studies on **2a** are displayed in Figure 1. Similar results (within experimental error) were obtained for **2b**. Three main features were observed in THF with 0.2 M [n-Bu₄N][PF₆] at 20 °C: two reversible one-electron oxidation waves at +0.64 and -0.90 V (relative to Cp₂Fe at 0.00 V) and an irreversible reduction at -2.28 V. In accord with these electrochemical data, we found that chemical reduction of **2a** with Na/Hg amalgam in THF led to decomposition to a brown, intractable tar. Oxidation reactions were more successful, however; e.g., eq 2. Analogous



oxidations occur when 2 is treated with AgOTf, HOTf, Me₃SiOTf (OTf = CF₃SO₃⁻), Co₂(CO)₈, and I₂ to give the triflate, Co(CO)₄⁻, and I₅⁻ salts, respectively. Tetraphenylboron salts are easily prepared by metathesis with NaBPh₄ in THF.

The oxidized species are diamagnetic, air- and moisture-stable, crystalline materials. They dissolve without decomposition in chloroform, acetone, acetonitrile, and THF. Conductivities in acetonitrile correspond to 1:1 electrolytes. Informative NMR data were obtained for all but the $Co(CO)_4^-$ derivative [2b][Co(CO)_4], which showed only broad, featureless peaks in the ¹H NMR spectrum. We attribute this phenomenon to the presence of traces of Co^{II} paramagnetic decomposition products in solution. No evidence for ion pairing¹⁰ was detected by IR spectroscopy. In addition to absorbtions due to 2b⁺, a single intense band for the $\nu(CO)$ (F₂) vibration of the T_d Co- $(CO)_4$ anion¹¹ was observed at 1895 cm⁻¹. In the ¹H NMR spectra of the remaining complexes, the two equivalent 2-MeC₆H₄ ligands show a set of four well-resolved multiplets for the four aromatic protons, and an unusually high-field singlet for the CH_3 group (δ ca. 0.5 ppm). This value is ca. 1.5-2.0 ppm higher than is typically observed for ligands of this type [e.g., 2.11 ppm for $Ru(2-MeC_6H_4)_4^6$], presumably due to through-space shielding from π -electron density in the benzyne ligand. The latter group gives rise to a set of three downfield shifted aromatic signals (ca. 7.5–9.0 ppm) and a singlet for the methyl protons at ca. 3.0 ppm. The phosphines are inequivalent, having two doublets for the methyl groups (in both 2a and 2b salts) by ¹H NMR and an AB quartet by ³¹P¹H NMR. Notable features in the ¹³C NMR spectrum are the two doublets of doublets at ca. 164 and 167 ppm due to splitting of the benzyne carbon (C-5, C-6) resonances by the inequivalent phosphines and the signal due to the ipso (C-1) carbons of the 2-MeC₆ H_4 ligands which appears as a pseudotriplet



Figure 2. ORTEP view of the cation in $[2a][I_6]$ with atom labeling scheme. Methyl groups on phosphorus have been omitted for clarity.

at ca. 191 ppm. No further splitting of these signals was revealed upon ¹H coupling. The ¹H and ³¹P{¹H} NMR spectra of [2a][OTf] were invariant over the temperature range 20–100 °C, indicating that rotation about the Rebenzyne bond is either nonexistent or slow on the NMR time scale.

The benzyne cations 2^+ are, like their neutral precursors, remarkably stable. They are unaffected by the following substrates: I₂ and HOTf (excess in THF, 60 °C, 1 day); PMe₃, CO, C₂H₄, C₂H₂, Me₃SiCCSiMe₃, H₂, and MeI (excess in CDCl₃, 60 °C, 1 day) and can be refluxed in acetone, acetonitrile, THF, or chloroform without decomposition. No reaction takes place when [2a][PF₆] is treated with t-BuNC (excess) at 20 °C; however, in refluxing THF a complex mixture of products is formed, the nature of which is still under investigation. Reaction of [2b][PF₆] with an excess of LiBEt₃H or Me₃SiCH₂MgCl in THF leads to reduction of the metal center and near quantitative formation of the neutral benzyne 2b.

Structure of $[\text{Re}(\eta^2-2-\text{MeC}_6\text{H}_3)(2-\text{MeC}_6\text{H}_4)_2-(\text{PMe}_3)_2][\text{I}_5]$ ([2a][I₅]). The basic configuration of the cation [2a] is analogous to that of the neutral molecule⁷ and is shown in Figure 2. The geometry can be described as trigonal-bipyramidal if the benzyne is assumed to occupy one coordination site, with the phosphines axial. The cation has an approximate mirror plane of symmetry coincident with the benzyne ligand and containing the metal, the two phosphorus atoms, and, in this case, one methyl carbon of each phosphine. Furthermore, the two PMe₃ groups are themselves related by an approximate mirror plane, which also contains the atoms of the two 2-MeC₆H₄ groups. The approximate $C_{2\nu}$ symmetry is then only destroyed by the methyl substituent on the benzyne ligand.

The benzyne ligand itself is bonded in a symmetrical manner, with the Re–C distances equal, within the limits of experimental error. Unfortunately, the rather high esd's for the geometry parameters of the organic ligands, due almost certainly to the presence of so many heavy atoms (Re and I), do not allow any detailed discussion of the geometries of either the benzyne or the 2-MeC₆H₄ ligands. However, the indications are that the Re–C distances to the benzyne carbons are shorter than those to the tolyl carbons. Selected bond lengths and angles are given in Table I, which also contains data for the neutral molecule.⁷ Again, detailed comparisons are thwarted by the large esd's, but there is no doubt that all Re–C distances for the cation are shorter than those for the neutral molecule.⁷ as

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Table I. Selected Bond Lengths (Å) and Angles (deg) for [2a][I₅] and the Related, Neutral Complex 2b^a

[2a][15] and the Related, Neutral Complex 20								
	$[2a][I_5]$	2b						
A. Cation								
(i) Bond Lengths								
Re-P(1)	2.435(5)	2.431 (4)						
Re-P(2)	2.421(5)	2.407(4)						
Re-C(11)	2.02 (2)	2.026(7)						
Re-C(12)	2.02(2)	2.046(7)						
Re-C(21)	2.08(1)	2.120 (7)						
Re -C(31)	2.09 (1)	2.115 (7)						
C(11)-C(12)	1.39 (2)	1.34(1)						
C(12) - C(13)	1.39 (2)	1.43(1)						
C(13) - C(14)	1.39(2)	1.38(1)						
C(14) - C(15)	1.44(2)	1.41(1)						
C(15)-C(16)	1.36 (2)	1.37(1)						
C(16)-C(11)	1.36(2)	1.41 (1)						
C(13)-C(17)	1.50(3)	1.49 (1)						
P-C(Me)	1.81 (1)-1.83	(1) 1.822 (11)-1.83	37 (5)					
C-C(tol)	1.33(3) - 1.43	(2) 1.35 (1)-1.42 (1)					
C(22)-C(27)	1.49 (2)	1.50(1)						
C(32)-C(33)	1.52(2)	1.50(1)						
(ii) Angles								
P(2)-Re-P(1)	159.6 (2)	153.5(1)						
C(21)-Re- $C(31)$	125.3 (6)	118.7 (3)						
C(11)-Re- $C(12)$	40.3 (6)	38.5 (2)						
P(1)-Re-C(12)	83.4 (6)	84.8 (3)						
P(2)-Re-C(11)	76.8 (5)	82.7 (3)						
P(1)-Re-C(21)	85.7 (4)	86.3 (3)						
P(1)-Re- $C(31)$	83.6 (4)	82.7 (3)						
P(2)-Re-C(21)	85.6 (4)	83.2 (3)						
P(2)-Re-C(31)	86.4 (4)	81.9 (3)						
Re-C(21)-C(22)	125(1)	120.1 (4)						
Re-C(21)-C(26)	116 (1)	124.6(5)						
Re-C(31)-C(32)	123 (1)	123.1(4)						
Re-C(31)-C(36)	117 (1)	121.3(5)						
B. Cation System								
$\mathbf{I}(1) = \mathbf{I}(0)$	(i) interatomic	LISTANCES	=)					
I(1) - I(2) I(0) - I(0)	3.038 (5)	I(1) - I(4) = 3.322 (-1)	5) El					
1(2)-1(3)	2.844 (5)	1(4)-1(5) 2.774 (5)					
1(1a)1(5)	3.481 (5)							

^a Data taken from ref 7. ^b I(1a) = I(1) × [1 - x, 2 - y, -0.5 + z].

would be expected. However, the Re–P distances are similar, and the absence of any shortening on changing from the neutral to the charged species may reflect some loss of π -back-bonding. The precise distribution of interligand angles are as might be expected. Thus, the C-(benzyne)–Re–P angle is larger on the side containing the methyl substituent, and the 2-MeC₆H₄ ligands are slightly tilted due to steric contact between the 2-MeC₆H₄ methyls and the benzyne ring.

The geometry of the I_5^- unit is different to those found in other structures, (which comprise two I_2 molecules linked by an I^- ion¹²), with an I_2 molecule associating with an unsymmetrical I_3^- ion in a V-shaped configuration (see Figure 3 and Table I). Further association into chains occurs via slightly longer contacts between I(1) of the $I_3^$ and terminal I(5) of the I_2 unit of a neighboring I_5 group.

We have also determined the structures of 2a and $[2a][BPh_4]$; however, due to twofold disorder of the benzyne, we consider the data to be of insufficient accuracy to report. Nevertheless, the gross structural features of these derivatives are clearly analogous to those of 2b and $[2a][I_5]$.

Summary and Conclusions. Under comparatively mild conditions, phosphine-induced ortho-hydrogen abstractions provide high-yield routes to new rhenium-benzyne derivatives. The steric bulk, rather than basicity, of





Figure 3. Packing diagram of the crystal structure of $[2a][I_5]$ viewed down the *a* axis.

the incoming phosphine appears to be more important in determining the success of the reaction. Compared with previously reported examples, the metal-benzyne linkage is remarkably inert. On the basis of ESR, NMR, and X-ray data, the Re-benzyne interaction is probably best described on the basis of a rhenacyclopropene-type structure with a delocalized, aromatic benzyne ring (structure III). Further studies on the chemistry of homoleptic aryls are in progress; e.g., the Mo analog of 2 is made similarly.



Experimental Section

All manipulations were performed under an atmosphere of argon by using dry, oxygen-free solvents. Microanalyses were by Pascher Laboratories or Imperial College. Spectrometers: IR, Perkin-Elmer 1720 (Nujol mulls, values in cm⁻¹); NMR, JEOL GSX 270 or FX 90Q and Bruker WM-250 (data in ppm relative to SiMe₄ (¹H, ¹³C) or 85% H₃PO₄ (³¹P) at 22 °C); mass, VG 7070 (70 eV); ESR, Varian E-12 (X-band, in benzene-d₆ at 22 °C). Cyclic voltammetry: OE-PP2 instrument with 0.2 M [n- Bu_4N [PF₆] in THF at 22 °C with platinum working, tungsten auxillary, and silver pseudo reference electrodes. Scan rates of 20-200 mV s⁻¹ were employed in all studies. Under these conditions, Cp_2Fe was oxidized at +0.85 V with $\Delta E_p = 90$ mV. This rather high value (theoretical = 59 mV) is presumably due to uncompensated resistance in solution.¹³ Melting points were determined in sealed capillaries under argon and are uncorrected. Conductivities were measured on a Data Scientific PTI-18 (0.01 M solutions in MeCN). MS data refer to the ion due to ¹⁸⁷Re; expected isotope envelopes were observed.

Re(η^2 -2-**MeC**₆**H**₃)(2-**MeC**₆**H**₄)₂(**PMe**₃)₂ (2a). Neat PMe₃ (0.46 cm³, 5.2 mmol) was added to a solution of Re(2-MeC₆**H**₄)₄⁶ (1.39 g, 2.52 mmol) in THF (40 cm³). After removal of volatiles, extraction into warm hexane (100 cm³), and filtration, the maroon solution was concentrated and cooled (-15 °C) to yield 1.40 g (91%) of the dark maroon product (mp 165–166 °C). Anal. Calcd for C₂₇H₃₉P₂Re: C, 53.1; H, 6.27; P, 10.2. Found: C, 53.2; H, 6.32; P, 10.4. IR: 3050 w, 1568 m, 1414 m, 1296 m, 1278 m, 1026 m, 1018 m, 982 m, 942 s, 851 m, 764 m, 732 s, 669 m, 640 m cm⁻¹. Magnetic moment: 1.60 (5) μ_B (Evans' method in toluene). ESR: 6-line pattern $g_{iso} = 2.040$, $A_{iso} = 0.0208$ cm⁻¹. Mass spectrum:

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m/e (relative intensity), 611 (M⁺, 68), 535 (M⁺ – PMe₃, 21), 441 (100), 459 (M⁺ – 2PMe₃, 13).

Re(η²-2-**MeC**₆**H**₃)(2-**MeC**₆**H**₄)₂(**PMe**₂**Ph**)₂ (2b). The procedure for **2a** was repeated by using PMe₂Ph (0.30 cm, 2.1 mmol) and **1** (0.18 g, 0.33 mmol). Workup as above gave **2b** as dark orange crystals (mp 148–150 °C) in 75% yield (0.18 g). Anal. Calcd for $C_{37}H_{42}P_2Re: C, 60.1; H, 5.76.$ Found: C, 60.1; H, 5.80. IR: 3052 w, 1566 s, 1325 m, 1292 m, 1275 m, 1027 w, 1010 m, 985 w, 942 m, 904 s, 837 w, 777 m, 736 s, 695 m, 640 w, 493 m. Mass spectrum: m/e (relative intensity) 735 (M⁺, 0.4), 598 (M⁺ – PMe₂Ph, 0.3), 459 (M⁺ – 2PMe₂Ph, 0.2) 57 (100).

 $[\mathbf{Re}(\eta^2 - 2 - \mathbf{MeC}_6\mathbf{H}_3)(2 - \mathbf{MeC}_6\mathbf{H}_4)_2(\mathbf{PMe}_3)_2][\mathbf{PF}_6] ([2a][\mathbf{PF}_6]).$ THF (20 cm³) was added to a mixture of 2a (0.13 g, 0.21 mmol) and Cp_2FePF_6 (0.70 g, 0.21 mmol). The red solution was evaporated and the residue washed with diethyl ether (30 cm^3) . The remaining solid was dissolved in THF (30 cm³), filtered, and concentrated to ca. 10 cm³. Cooling to -15 °C overnight afforded the product as brown crystals (mp 218-219 °C) of the THF solvate $(0.6 \text{ equiv by } {}^{1}\text{H NMR})$ in 93% yield (0.15 g). Anal. Calcd for C₂₇H₃₈F₆P₃Re·(THF)_{0.6}: C, 44.2; H, 5.52; F, 14.2. Found: C, 44.2; H, 5.37; F, 13.8. THF in the above complex may be removed by crystallization from dichloromethane/diethyl ether. IR: 1598 w, 1569 m, 1425 m, 1307 m, 1292 m, 1170 w, 1065 m, 1025 m, 952 s, 840 s, 784 m, 748 s, 671 m, 641 m, 558 s. ¹H NMR (250 MHz, acetone-d₆): δ 0.53 (s, 6 H, 2-MeC₆H₄), 1.77 (m, THF), 1.84 (d, $J_{\rm PH} = 7$ Hz, 9 H, PMe₃), 1.85 (d, $J_{\rm PH} = 7$ Hz, 9 H, PMe₃), 2.42 (m, THF), 3.09 (s, 3 H, 2- MeC_6H_3), 6.75 (t, J = 7 Hz, 2H), 6.93 (d, J = 7 Hz, 2 H), 7.43 (t, J = 7 Hz, 2 H), 7.82 (d, J = 6 Hz, 1 H), 7.97 (t, J = 7 Hz, 1 H), 8.76 (d, J = 7 Hz, 1 H). ¹³C{¹H} NMR (dichloromethane- d_2 , 69.7 MHz): δ 15.32 (d, J_{PC} = 34 Hz, PMe₃), 16.36 (d, $J_{PC} = 33$ Hz, PMe₃), 23.49 (s, $2-MeC_6H_3$), 26.65 (s, $2 - MeC_6H_4$, 123.6 (t, $J_{PC} = 3.6Hz$, $2 - MeC_6H_4$), 123.8 (d, $J_{PC} = 2.5$ Hz, 2-MeC₆H₃), 125.4 (br, 2-MeC₆H₄), 125.5 (d, $J_{PC} = 2.4$ Hz, $2-MeC_6H_4$), 133.1 (d $J_{PC} = 2.5$ Hz, $2-MeC_6H_4$), 133.4 (t, $J_{PC} = 2.5$ Hz, 2-MeC₆H₄), 137.7 (dd, $J_{PC} = 7.3$, 2.4Hz, 2-MeC₆H₃), 138.4 (s, 2-MeC₆H₃), 138.5 (s, 2-MeC₆H₃), 164.4 (dd, $J_{PC} = 24$, 3 Hz, 2-MeC₆H₃), 164.4 (dd, J_{PC} = 24, 3 Hz, 2-MeC₆H₃), 1 MeC_6H_3 , 167.4 (dd, $J_{PC} = 29$, 3 Hz, 2-Me C_6H_3 , 189.8 ("t", $J_{PC} = 10$ Hz, 2-Me C_6H_4). ³¹P{¹H} NMR (chloroform-d, 36.3 MHz): δ 22.9, 30.3 (AB quartet, J = 128 Hz). Conductivity: $\Lambda_{\rm M} = 110$ Ω^{-1} cm² mol⁻¹.

 $[\mathbf{Re}(\eta^{2}\text{-}2\text{-}\mathbf{MeC}_{6}\mathbf{H}_{3})(2\text{-}\mathbf{MeC}_{6}\mathbf{H}_{4})_{2}(\mathbf{PMe}_{3})_{2}][\mathbf{BPh}_{4}] ([2a][\mathbf{BPh}_{4}]). Compound [2a][\mathbf{PF}_{6}] (0.10 g, 0.13 mmol) and NaBPh_{4} (0.2 g, excess) were stirred for 8 h in THF (10 cm³). After removal of volatiles in vacuo, the brown residue was extracted into dichloromethane; filtration, concentration, and cooling gave brown crystals (0.11 g, 89%), mp 188–192 °C. Anal. Calcd for C_{51}H_{58}BP_{2}Re: C, 65.8; H, 6.39. Found: C, 65.6; H, 6.37. IR: 1585 w, 1569 m, 1420 m, 1288 m, 1268 w, 1247 m, 1152 m, 1025 m, 945 s, 848 m, 744 m, 732 s, 709 s, 612 m, 602 m. ¹H NMR (dichloromethane-d_{2}, 250 MHz): <math>\delta$ 0.46 (s, 6 H, 2-MeC_{6}H_{4}), 1.68 ("d", J = 10 Hz, 18 H, PMe_{3}), 2.95 (s, 3 H, 2-MeC_{6}H_{3}), 6.57 (d, J = 9 Hz, 2 H), 6.75 (t, J = 7 Hz, 2 H), 7.30 (br m, 8 H), 7.39 (t, J = 7 Hz, 2 H), 7.63 (d, J = 7 Hz, 2 H), 7.78 (t, J = 8 Hz, 1 H), 8.29 (d, J = 7 Hz, 1 H). ³¹P{¹H} NMR (dichloromethane-d_{2}, 36.3 MHz): δ 18.8, 25.7 (AB quartet, J = 134 Hz).

[Re(η^2 -2-MeC₆H₃)(2-MeC₆H₄)₂(PMe₃)₂][OTf] ([2a][OTf]). HOTf (0.014 cm³, 0.32 mmol) was added to a diethyl ether solution of 2a (0.10 g, 0.16 mmol in 10 cm³). After the solution was stirred for 30 min, the brown precipitate was filtered off and recrystallized from dichloromethane/diethyl ether to afford brown crystals (mp 209–210 °C) in 84% yield (0.10 g). Anal. Calcd for C₂₈H₃₈F₃P₂O₃ReS: C, 46.1; H, 5.39. Found: C, 45.7; H, 5.09. IR: 1598 w, 1568 m, 1422 m, 1308 w, 1286 sh, 1261 s, 1224 m, 1150 s, 1032 s, 950 s, 865 m, 745 s, 731 sh, 638 s, 572 w, 517 m. ¹H NMR (chloroform-d, 90 MHz): δ 0.44 (s, 6 H), 1.73 (d, $J_{PH} = 9$ Hz, 9 H), 1.76 (d, $J_{PH} = 9$ Hz, 9 H), 2.98 (s, 3 H), 6.5–6.8 (m, 6 H), 7.10 (d, J = 7 Hz, 2 H), 7.60 (d, J = 7 Hz, 1 H), 7.83 (t, J = 7 Hz, 1 H), 8.51 (d, J = 7 Hz, 1 H). ³¹P{¹H} NMR (chloroform-d, 36.3 MHz): δ 17.3, 25.0 (AB quartet, J = 131 Hz).

 $[\text{Re}(\eta^2-2-\text{MeC}_6H_3)(2-\text{MeC}_6H_4)_2(\text{PMe}_3)_2][I_5]$ ([2a][I₅]). Excess iodine (ca. 100 mg) was added to a THF solution (10 cm³) of 2a (0.06 g, 0.1 mmol). The orange solution was evaporated in vacuo; the residue was extracted into dichloromethane (10 cm³) and the solution filtered. After concentration to ca. 3 cm³, diethyl ether was added (5 cm³) and the mixture was allowed to stand for 2 days. Large brown crystals (mp 202–204 °C) were collected by filtration (0.06 g, 60%). From elemental analysis, the material prepared by this method appears to be a mixture of I_5^- and I_3^- salts. Anal. Calcd for $C_{27}H_{39}I_4P_2Re$: C, 29.0; H, 3.51; I, 45.4. Found: C, 30.2; H, 3.44; I, 47.4. The crystal chosen for X-ray diffraction was evidently the I_5^- salt. IR: 1597 w, 1567 m, 1409 m, 1285 m, 1158 w, 1043 m, 1024 m, 943 s, 857 m, 779 m, 747 s, 707 w, 641 m, 442 w. ¹H NMR (chloroform-d, 250 MHz): 0.48 (s, 6 H), 1.77 (d, $J_{PH} = 7$ Hz, 9 H), 1.80 (d, $J_{PH} = 7$ Hz, 9 H), 3.03 (s, 3 H), 6.63 (d, J = 8 Hz, 2 H), 6.68 (t, J = 7 Hz, 2 H), 7.14 (d, J = 7 Hz, 2 H), 7.43 (t, J = 7 Hz, 2 H), 7.68 (d, J = 7 Hz, 1 H), 7.93 (t, J = 7 Hz, 1 H), 8.49 (d, J = 7 Hz, 1 H). ³¹P₁¹H NMR (chloroform-d, 36.3 MHz): δ 17.4, 24.5 (AB quartet, J = 133 Hz).

 $[\text{Re}(\eta^2 - 2 - \text{MeC}_6\text{H}_3)(2 - \text{MeC}_6\text{H}_4)_2(\text{PMe}_2\text{Ph})_2][\text{PF}_6] ([2b][\text{PF}_6]).$ This was prepared as for $[2a][PF_6]$ by using 2b; yield 92%, dark brown prisms (mp 186-187 °C). Anal. Calcd for C₃₇H₄₂F₆P₃Re: C, 50.5; H, 4.81. Found: C, 50.2; H, 4.79. IR: 1600 w, 1568 m, 1317 w, 1302 m, 1284 m, 1102 m, 1025 m, 947 m, 908 s, 878 m, 841 s, 743 s, 702 m, 558 s, 493 w, 436 w. ¹H NMR (chloroform-d, 250 MHz): δ 0.56 (s, 6 H, 2-MeC₆H₄), 1.99 (d, J_{PH} = 9 Hz, 6 H, PMe_2Ph), 2.04 (d, $J_{PH} = 9$ Hz, 6 H, PMe_2Ph), 2.59 (s, 3 H, 2- $MeC_{6}H_{3}$), 5.98 (d, J = 7 Hz, 2 H, $PMe_{2}Ph$), 6.68 (t, J = 8 Hz, 2 H, PMe_2Ph), 6.85 ("q", J = 7 Hz, 4 H, 2-MeC₆H₄), 7.11 (t, J =7 Hz, 2 H, PMe₂Ph), 7.27 (m, 6 H), 7.44 (m, 2 H, 2-MeC₆H₄), 7.56 $(d, J = 7 Hz, 1 H, 2-MeC_6H_3), 7.79 (t, J = 7 Hz, 1 H, 2-MeC_6H_3),$ 8.36 (d, J = 7 Hz, 1 H, 2-MeC₆H₃). ¹³C{¹H} NMR (chloroform-d, 69.7 MHz): 14.45 (d, $J_{\rm PH}$ = 35 Hz, PMe_2Ph), 15.74 (d, $J_{\rm PC}$ = 34 Hz, PMe₂Ph), 23.14 (s, 2-MeC₆H₃), 26.63 (s, 2-MeC₆H₄), 124-138 $(2-\text{Me}C_6\text{H}_3, 2-\text{Me}C_6\text{H}_4, \text{PMe}_2Ph)$, 163.8 (br d, J = 28 Hz, 2- $MeC_{6}H_{3}$), 167.6 (br d, J = 30 Hz, 2- $MeC_{6}H_{3}$), 189.2 ("t", J = 10Hz, 2-MeC₆H₄). ³¹P{¹H} NMR (chloroform-d, 36.3 MHz): δ 20.7, 25.4 (AB quartet, J = 133 Hz).

 $[\text{Re}(\eta^2 - 2 - \text{MeC}_6\text{H}_3)(2 - \text{MeC}_6\text{H}_4)_2(\text{PMe}_2\text{Ph})_2][\text{OTf}]$ ([2b]-[OTf]). (a) From $2b + Me_3SiOTf$. A solution of 2b (0.10 g, 0.14 mmol) and Me₃SiOTf (0.026 cm³, 0.14 mmol) was warmed to 40 °C for 2 h in THF (10 cm³). Addition of hexane (50 cm³) gave a pink precipitate; recrystallization from dichloromethane/diethyl ether gave brown crystals (mp 179-182 °C) in 50% yield (0.06 g). Anal. Calcd for C₃₈H₄₂F₃O₃P₂ReS: C, 51.6; H, 4.79. Found: C, 51.7; H, 4.73. IR: 1590 w, 1568 m, 1266 s, 1223 m, 1151 m, 1101 m, 1032 s, 947 m, 991 s, 752 sh, 743 m, 637 s, 517 w, 491 w. $\,^1\!\mathrm{H}$ NMR (chloroform-d, 270 MHz): $\,\delta$ 0.55 (s, 6 H), 2.00 (d, J_{PH} = 9 Hz, 6 H), 2.11 (d, J_{PH} = 9 Hz, 6 H), 2.56 (s, 3 H), 5.97 (d, J = 8 Hz, 2 H), 6.65 (t, J = 8 Hz, 2 H), 6.80 (t, J = 7 Hz, 2 H), 6.89 (t, J = 7 Hz, 2 H), 7.09 (t, J = 8 Hz, 2 H), 7.23 (m, 8 H), 7.41 (m, 2 H), 7.55 (d, J = 7 Hz, 1 H), 7.86 (t, J= 7 Hz, 1 H), 8.57 (d, J = 7 Hz, 1 H). ³¹P{¹H} NMR (chloroform-d, 36.3 MHz): δ 18.0, 23.6 (AB quartet, J = 133 Hz). Conductivity: $\Lambda_{\rm M} = 103 \ \Omega^{-1} \ {\rm cm}^2 \ {\rm mol}^{-1}.$

(b) From 2b + AgOTf. THF (10 cm^3) was added to a mixture of 2b (0.10 g, 0.14 mmol) and AgOTf (0.035 g, 0.14 mmol). After the solution was stirred for 15 min, the volatiles were removed by vacuum transfer and the brown residue was extracted with dichloromethane (20 cm^3) . Filtration, concentration, and cooling (-15 °C) gave 0.11 g (91%) of dark brown crystals.

[Re(η^2 -2-MeC₆H₃)(2-MeC₆H₄)₂(PMe₂Ph)₂][Co(CO)₄] ([2b][Co(CO)₄]). A hexane solution of Co₂(CO)₈ (0.047 g, 0.14 mmol in 20 cm³) was added to a hexane solution of 2b (0.10 g, 0.14 mmol in 10 cm³). The maroon crystals that precipitated were filtered off after 8 h and recrystallized from THF/diethyl ether to afford large dark brown crystals (mp 135–136 °C) of the product (0.08 g, 63%). Anal. Calcd for C₄₁H₄₂CoP₂O₄Re: C, 54.4; H, 4.67. Found: C, 54.1; H, 4.65. IR: 1895 s, 1601 w, 1570 m, 1548 w, 1284 m, 1101 m, 1026 m, 945 m, 911 s, 839 m, 771 m, 739 s, 699 m, 642 m, 552 s, 490 m, 431 m. Magnetic moment: ≤0.3 μ_B (Evans' method in acetonitrile). Conductivity: Λ_M = 93 Ω⁻¹ cm² mol⁻¹.

Reaction of [2b][PF₆] with LiBEt₃H. A THF solution (10 cm³) of [2b][PF₆] (0.10 g, 0.11 mmol) and LiBEt₃H (0.11 cm³ of a 1 M solution in THF) was stirred overnight. After evaporation and extraction into hexane (20 cm³), the red filtrate was concentrated to ca. 2 cm³ and cooled (-15 °C) to give 0.06 g (74%) of dark red crystalline 2b (by IR and mp).

Reaction of [2b][PF₆] with Me_3SiCH_2MgCl. A solution of Me_3SiCH_2MgCl in THF (0.085 cm³ of a 1.2 M solution) was added to [**2b**][PF₆] (0.09 g, 0.1 mmol) in THF (10 cm³). The red solution was stirred overnight and evaporated, and the residue was ex-

Table II. Fractional Atomic Coordinates $(\times 10^4)$ and Equivalent Isotropic Temperature Factor Coefficients^a $(\times 10^3)$ for [2a][1.]

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		x	У	z	$U, Å^2$
	Re	1974.3 (2)	1604.1 (3)	0.0	30.2 (1)
	I(1)	5581.4 (6)	7858.8 (9)	-344.7(10)	68.2 (4)
	I(2)	4063.5 (5)	7149.2 (7)	-626.2 (8)	48.8 (3)
	I(3)	2668.6(7)	6372.9 (9)	-831.0 (10)	64.0 (4)
	I(4)	5278.9 (7)	9550.3 (10)	-1942.8 (11)	73.9 (5)
	I(5)	4870.9 (7)	10798.9 (9)	-3365.5(12)	78.1 (5)
	P(1)	2737(2)	200 (3)	156 (4)	57 (1)
	P(2)	1254 (2)	2971 (2)	446 (3)	37 (1)
	C(1)	2916 (12)	-141 (16)	1377 (19)	90 (10)
	C(21)	233 (10)	-907 (12)	-255 (19)	87 (10)
	C(3)	3616 (8)	335 (13)	-389 (18)	84 (8)
	C(4)	1565 (8)	4125 (8)	31 (14)	53 (5)
	C(5)	313 (8)	2916 (12)	130 (15)	66 (6)
	C(6)	1239 (9)	3136 (10)	1725(11)	53 (5)
	C(11)	1597 (9)	2085 (10)	-1244 (11)	53 (5)
	C(12)	2051 (8)	1313 (11)	-1389 (12)	50 (5)
	C(13)	2194 (9)	958 (14)	-2281 (11)	58 (6)
	C(14)	1805 (15)	1422(17)	-2979 (16)	90 (9)
	C(15)	1365 (12)	2251(16)	-2811 (13)	78 (8)
	C(16)	1262 (10)	2602(11)	-1929 (11)	56 (5)
	C(17)	2654(14)	130 (16)	-2586 (16)	94 (8)
	C(21)	2826 (6)	2366 (10)	570(12)	42 (5)
	C(22)	3278 (8)	3008 (10)	55 (16)	58 (5)
	C(23)	3754(10)	3562 (12)	594 (16)	70 (7)
	C(24)	3828(11)	3457(13)	1521 (19)	77 (8)
	C(25)	3451 (9)	2797 (13)	2015 (15)	66 (7)
	C(26)	2922 (8)	2284(12)	1560 (14)	59 (6)
	C(27)	3215 (12)	3115(16)	-986 (17)	82 (8)
	C(31)	1248(7)	775 (9)	770 (9)	36 (4)
	C(32)	706(7)	235 (9)	343 (10)	34 (4)
	C(33)	237(7)	-319 (11)	928 (12)	49 (5)
	C(34)	359 (10)	-360 (10)	1889 (11)	61 (6)
	C(35)	909 (9)	165 (11)	2287(11)	52 (6)
	C(36)	1331 (8)	748 (9)	1722(10)	44 (4)
	C(37)	547 (9)	232 (13)	-710 (12)	60 (6)

^a According to Hamilton (Acta Crystallogr. 1959, 12, 609-610).

tracted into hexane (20 cm^3) . Red crystals of **2b** were obtained by concentration and cooling of this solution (0.06 g, 80%).

X-ray Crystal Structure Determination of $[2a][I_5]$. Crystals suitable for X-ray work were grown from dichloromethane/diethyl ether as dark brown needles. The specimen used for the structural work had dimensions $0.22 \times 0.30 \times 0.70$ mm. Following preliminary photography, the orientation matrix and cell dimensions were obtained by using standard SEARCH and INDEX routines on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.710$ 69 Å) and refined by using setting angles for 25 well-spaced reflections with 9.7 $\leq \theta \leq 17.4^{\circ}$. The crystal system was found to be orthorhombic, with space group *Pna2*₁, and cell dimensions a = 18.735 (2) Å, b = 13.954 (5) Å, c = 14.193 (2) Å, V = 3710.6 Å³, M_r 1246.22 Z = 4, $D_{calcd} = 2.23$ g cm⁻³, $\mu = 73.0$ cm⁻¹, F(000) = 2284 at T = 291 K

Intensity data were recorded by using the $\omega/2\theta$ scan technique with $1.5 \le \theta \le 25^{\circ}$, $h = 0 \rightarrow 22$, $k = 0 \rightarrow 16$, $l = 0 \rightarrow 16$, scan width $\omega = 0.85 + 0.35 \tan \theta$, and variable scan speed $1.34 - 6.7 \deg \min^{-1}$ to achieve $I \ge 33\sigma(I)$ subject to $t_{max} = 60$ s. A total of 3681 data were measured to which 3413 were unique and 2836 observed [I > 1.5 $\sigma(I)$]. The data were corrected for absorption empirically; relative maximum and minimum transmission factors were 1.00 and 0.67, respectively. The structure was solved by direct methods (SHELXS 86)¹⁴ and developed and refined by Fourier and full matrix least squares procedures (SHELX 76).¹⁵ All non-hydrogen atoms were refined anisotropically; hydrogens were not included. The final R and R_w values were 0.0296 and 0.0417, respectively, for 315 parameters and weights = $[\sigma^2(F_0) + 0.0002F_0^2]^{-1}$. The largest Δ/σ was 0.35 and the minimum/maximum values of $\Delta\rho$ were -0.9/0.7 e Å⁻³, respectively. The final coordinates are listed in Table II. Refinement of an inverted set of coordinates gave R and R_w values of 0.0361 and 0.0452, respectively, confirming the original assignment.

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Registry No. 1, 117407-56-4; 2a, 117407-50-8; [2a][PF₆], 117407-53-1; [2a][BPh₄], 117467-85-3; [2a][OTf], 117467-86-4; [2a][I₅], 117467-87-5; 2b, 117407-51-9; [2b][PF₆], 117407-55-3; [2b][OTf], 117467-88-6; [2b][Co(CO)₄], 117467-89-7.

Supplementary Material Available: Tables of U_{ij} values and bond lengths and angles (2 pages); a listing of F_o/F_c values (17 pages). Ordering information is given on any current masthead page.

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Deprotonation and Anionic Rearrangement in $CpRe(NO)(R)(PPh_3)$ (R = CHO, CH₃)

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The mechanism of migration of the CHO ligand from the metal to the deprotonated cyclopentadienyl ring in $[(\eta^5-C_5H_4)Re(NO)(CHO)(PPh_3)]^-$ is analyzed from a theoretical point of view. Total energy values for all stable molecules and possible intermediates involved in the reaction are used to determine the lowest energy path. The results are then explained by examining the changes in molecular orbitals occurring during the migration. The fact that alkyl ligands, on the other hand, do not undergo migration to the cyclopentadienyl ligand is also examined.

Introduction

Gladysz and co-workers have recently observed a series of deprotonation reactions involving rhenium complexes of the kind $CpRe(R)(NO)(PPh_3)$, where $R = C(O)CH_3$, $C(O)C_6H_5$, $C(O)CH_2C_6H_5$, C(O)H, H, CH_3CHCN , (C- $H_3)_2CH$, H_2CH , $H_2CC_6H_5$, and $H_2CCH=CH_2$.¹⁻⁶ Some

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