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 rapidily 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**).

Acknowledgment. We wish to thank Prof. Michael Green (King's College, University of London) for valuable discussions. We are grateful for the support of this work by the National Science Foundation (CHE86-03728) and by NATO.

Registry No. **1**, 74380-97-5; **2**, 76800-62-9; $[CpMo(C_2Me_2)_2]_2$, 118299-17-5.

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 $[Re(\eta^2\text{-}2\text{-}MeC_6H_3)(2\text{-}MeC_6H_4)_2(PMe_3)_2][I_5]$

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The paramagnetic benzyne complexes $Re(\eta^2\text{-}2\text{-}MeC_6H_3)(2\text{-}MeC_6H_4)_2(PMe_2R)_2$ (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 $Re(2\text{-}MeC_6H_4)_4$ (**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., $LiBEt_3H$, Me_3SiCH_2MgCl, 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($2\text{-}MeC_6H_4$) 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, d^0 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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(1) (a) McLain, S. J.; Schrock, R. R.; Sharp, P. R; Churchill, M. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 263. (b) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 1697.

(2) (a) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7411. (b) Buchwald, S. L.; Lucas, E. A.; Dewan, J. C. *Ibid.* **1987**, *109*, 4396. (c) Buchwald, S. L.; Watson, B. T.; Lum, R. T.; Nugent, W. A. *Ibid.* **1987**, *109*, 7137.

(3) Bartlett, R. A.; Power, P. P.; Shoner, S. C. *J. Am. Chem. Soc.* **1988**, *110*, 1966.

(4) Bennett, M. A.; Hambley, T. W.; Roberts, N. K.; Robertson, G. B. *Organometallics* **1985**, *4*, 1992.

(5) (a) Chamberlain, L. R.; Kerschner, J. L.; Rothwell, A. P.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 6471. (b) Schock, L. E.; Brock, C. P.; Marks, T. J. *Organometallics* **1987**, *6*, 232. (c) Bockel, C. P.; Teuben, J. H.; de Liefde Meijer, H. J. *J. Organomet. Chem.* **1974**, *81*, 371. (d) Berkovich, E. G.; Shur, V. G.; Vol'pin, M. E.; Lorenz, B. E.; Rummel, S.; Wahren, M. *Chem. Ber.* **1980**, *113*, 70. (e) Erker, G.; Kropp, K. J. *J. Am. Chem. Soc.* **1979**, *101*, 3659. (f) Erker, G.; Kropp, K. J. *Organometallics* **1982**, *1*, 1246. (g) Erker, G. *J. Organomet. Chem.* **1977**, *134*, 189. (h) Miller, F. D.; Sanner, R. D. *Organometallics* **1988**, *7*, 818.

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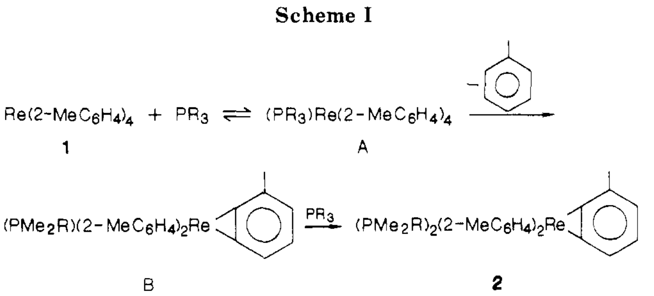
Scheme I

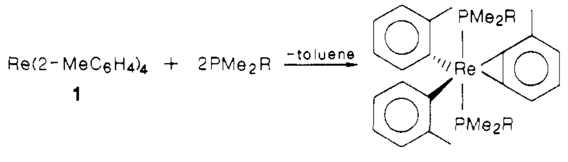


for instance, appears to be facile; metal–benzyne bonds have been cleaved quite readily by reagents such as MeOH, MeI, and I_2.

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, 11-electron rhenium(IV) (d^3) tetraaryl, $Re(2\text{-}MeC_6H_4)_4$[6] (1). A preliminary account has appeared.[7]

Results and Discussion

Preparation and Properties of $Re(\eta^2\text{-}2\text{-}MeC_6H_3)(2\text{-}MeC_6H_4)_2(PMe_2R)_2$. Addition of phosphine (PMe_3 or PMe_2Ph, ≥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 PMe_3; −15 °C with PMe_2Ph) to yield a deep maroon-red solution. Benzyne complexes $Re(\eta^2\text{-}2\text{-}MeC_6H_3)(2\text{-}MeC_6H_4)_2(PMe_2R)_2$ (**2a**, R = Me; **2b**, R = Ph) were isolated in high yields after removal of volatiles and crystallization from hexane (eq 1). The purple intermediate 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_8D 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*-Pr_3 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 $PMePh_2$, PPh_3, PCy_3, and $P(SiMe_3)_3$; reaction with dmpe in hexane gave an amorphous orange material that was insoluble in common organic solvents. Pyridine and NMe_3 did not react with 1; CO and *t*-BuNC reacted rapidly, but the complex mixtures of products have not yet been identified.



(1)

2a, R = Me
b, R = Ph

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 six-line ESR spectra due to coupling of the electron with Re (^{187}Re, 63%, $I = {}^5/_2$; ^{185}Re, 37%, $I = {}^5/_2$). 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]

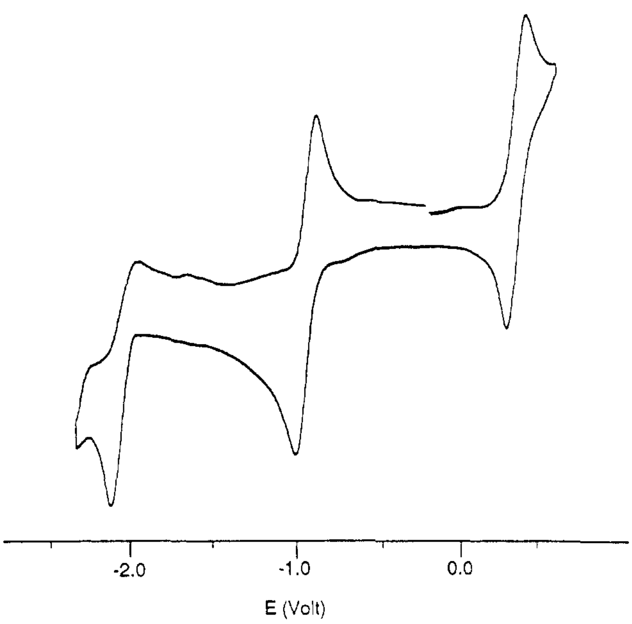
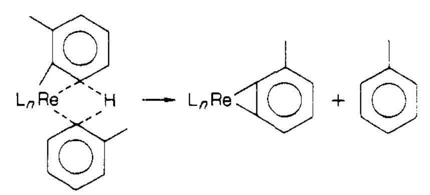


Figure 1. Cyclic voltammogram of **2a** in THF 0.2 M [$n\text{-}Bu_4N$][PF_6] at 50 mV s^{-1}, referenced to Cp_2Fe at 0.00 V.

Scheme II



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*-Pr_3, PCy_3, PPh_3, $P(SiMe_3)_3$] 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 H_2. 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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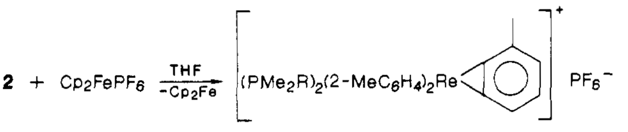
[6] Savage, P. D.; Wilkinson, G.; Hussain, B.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1988**, 669.

[7] Arnold, J.; Wilkinson, G.; Hussain, B.; Hursthouse, M. B. *J. Chem. Soc., Chem. Commun.* **1988**, 704.

straction via a four-center transition state (Scheme II). Related abstraction processes are common in d^0 systems.[8] Note that in the analogous osmium system, $Os(2\text{-}MeC_6H_4)_4$ 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 $[n\text{-}Bu_4N][PF_6]$ at 20 °C: two reversible one-electron oxidation waves at +0.64 and −0.90 V (relative to Cp_2Fe 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, Me_3SiOTf ($OTf = CF_3SO_3^-$), $Co_2(CO)_8$, and I_2 to give the triflate, $Co(CO)_4^-$, and I_5^- salts, respectively. Tetraphenylboron salts are easily prepared by metathesis with $NaBPh_4$ in THF.



[2][PF6] (2)

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 $[\mathbf{2b}][Co(CO)_4]$, 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 pairing[10] was detected by IR spectroscopy. In addition to absorbtions due to $\mathbf{2b}^+$, a single intense band for the $\nu(CO)$ (F_2) vibration of the T_d $Co(CO)_4^-$ anion[11] was observed at 1895 cm^{-1}. In the ^1H NMR spectra of the remaining complexes, the two equivalent $2\text{-}MeC_6H_4$ 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 $Ru(2\text{-}MeC_6H_4)_4{}^6$], 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 $^{31}P\{^1H\}$ NMR. Notable features in the ^{13}C 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 $2\text{-}MeC_6H_4$ ligands which appears as a pseudotriplet at ca. 191 ppm. No further splitting of these signals was revealed upon ^1H coupling. The ^1H and $^{31}P\{^1H\}$ NMR spectra of [**2a**][OTf] were invariant over the temperature range 20–100 °C, indicating that rotation about the Re–benzyne bond is either nonexistent or slow on the NMR time scale.

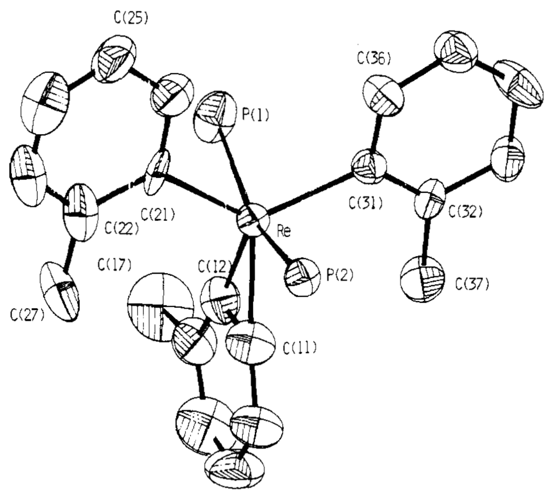


Figure 2. ORTEP view of the cation in $[\mathbf{2a}][I_5]$ with atom labeling scheme. Methyl groups on phosphorus have been omitted for clarity.

The benzyne cations $\mathbf{2}^+$ are, like their neutral precursors, remarkably stable. They are unaffected by the following substrates: I_2 and HOTf (excess in THF, 60 °C, 1 day); PMe_3, CO, C_2H_4, C_2H_2, $Me_3SiCCSiMe_3$, H_2, and MeI (excess in $CDCl_3$, 60 °C, 1 day) and can be refluxed in acetone, acetonitrile, THF, or chloroform without decomposition. No reaction takes place when $[\mathbf{2a}][PF_6]$ 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 $[\mathbf{2b}][PF_6]$ with an excess of $LiBEt_3H$ or Me_3SiCH_2MgCl in THF leads to reduction of the metal center and near quantitative formation of the neutral benzyne **2b**.

Structure of $[Re(\eta^2\text{-}2\text{-}MeC_6H_3)(2\text{-}MeC_6H_4)_2(PMe_3)_2][I_5]$ ($[\mathbf{2a}][I_5]$). The basic configuration of the cation [**2a**] is analogous to that of the neutral molecule[7] 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 PMe_3 groups are themselves related by an approximate mirror plane, which also contains the atoms of the two $2\text{-}MeC_6H_4$ groups. The approximate C_{2v} 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 $2\text{-}MeC_6H_4$ 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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(8) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203 and references therein.

(9) Arnold, J.; Wilkinson, G.; Hussain, B.; Hursthouse, M. B. *Organometallics*, submitted for publication.

(10) (a) Bockman, T. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1988**, *110*, 1294. (b) Tilley, T. D.; Anderson, R. A. *J. Chem. Soc., Chem. Commun.* **1981**, 985.

(11) Edgell, W. F.; Hegde, S.; Barbetta, A. *J. Am. Chem. Soc.* **1978**, *100*, 1406.

Table I. Selected Bond Lengths (Å) and Angles (deg) for [2a][I_5] and the Related, Neutral Complex 2b[a]

	[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)–1.837 (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			
	(i) Interatomic Distances			
I(1)–I(2)	3.038 (5)		I(1)–I(4)	3.322 (5)
I(2)–I(3)	2.844 (5)		I(4)–I(5)	2.774 (5)
I(1a)···I(5)[b]	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-MeC_6H_4 ligands are slightly tilted due to steric contact between the 2-MeC_6H_4 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^- ion[12]), 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 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.

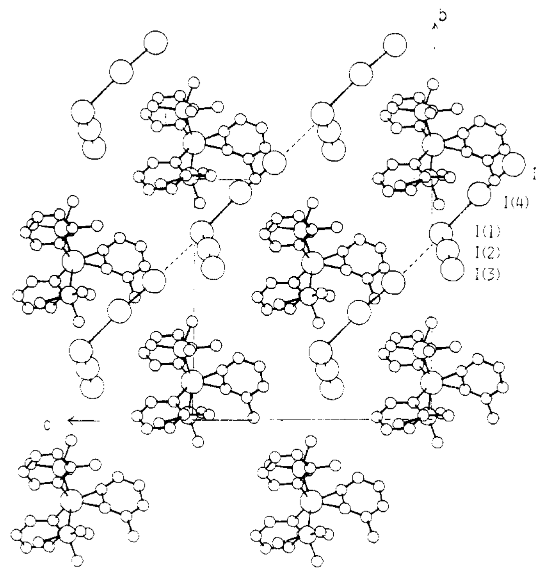
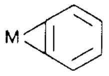


Figure 3. Packing diagram of the crystal structure of [**2a**][I_5] viewed down the *a* axis.



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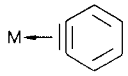
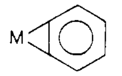
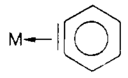


II



III



IV

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 $SiMe_4$ (^1H, ^{13}C) or 85% H_3PO_4 (^{31}P) at 22 °C); mass, VG 7070 (70 eV); ESR, Varian E-12 (X-band, in benzene-d_6 at 22 °C). Cyclic voltammetry: OE-PP2 instrument with 0.2 M [n-Bu_4N][PF_6] 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 ΔE_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 ^{187}Re; expected isotope envelopes were observed.

Re(η^2-2-MeC_6H_3)(2-MeC_6H_4)$_2$(PMe_3)$_2$ (2a). Neat PMe_3 (0.46 cm^3, 5.2 mmol) was added to a solution of Re(2-MeC_6H_4)$_4$[6] (1.39 g, 2.52 mmol) in THF (40 cm^3). After removal of volatiles, extraction into warm hexane (100 cm^3), 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 $C_{27}H_{39}P_2Re$: 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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[12] See: Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; p. 577.

[13] Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; p 230.

m/e (relative intensity), 611 (M$^+$, 68), 535 (M$^+$ – PMe$_3$, 21), 441 (100), 459 (M$^+$ – 2PMe$_3$, 13).

Re(η^2-2-MeC$_6$H$_3$)(2-MeC$_6$H$_4$)$_2$(PMe$_2$Ph)$_2$ (2b). The procedure for **2a** was repeated by using PMe$_2$Ph (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$_2$Re: 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$^+$ – PMe$_2$Ph, 0.3), 459 (M$^+$ – 2PMe$_2$Ph, 0.2) 57 (100).

[Re(η^2-2-MeC$_6$H$_3$)(2-MeC$_6$H$_4$)$_2$(PMe$_3$)$_2$][PF$_6$] ([2a][PF$_6$]). THF (20 cm^3) was added to a mixture of **2a** (0.13 g, 0.21 mmol) and Cp$_2$FePF$_6$ (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 cm^3), filtered, and concentrated to ca. 10 cm^3. Cooling to –15 °C overnight afforded the product as brown crystals (mp 218–219 °C) of the THF solvate (0.6 equiv by ^{1}H NMR) in 93% yield (0.15 g). Anal. Calcd for C$_{27}$H$_{38}$F$_6$P$_3$Re·(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. ^{1}H NMR (250 MHz, acetone-*d*$_6$): δ 0.53 (s, 6 H, 2-*Me*C$_6$H$_4$), 1.77 (m, THF), 1.84 (d, J_{PH} = 7 Hz, 9 H, PMe$_3$), 1.85 (d, J_{PH} = 7 Hz, 9 H, PMe$_3$), 2.42 (m, THF), 3.09 (s, 3 H, 2-*Me*C$_6$H$_3$), 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). ^{13}C{^{1}H} NMR (dichloromethane-*d*$_2$, 69.7 MHz): δ 15.32 (d, J_{PC} = 34 Hz, PMe$_3$), 16.36 (d, J_{PC} = 33 Hz, PMe$_3$), 23.49 (s, 2-*Me*C$_6$H$_3$), 26.65 (s, 2-*Me*C$_6$H$_4$), 123.6 (t, J_{PC} = 3.6Hz, 2-Me*C*$_6$H$_4$), 123.8 (d, J_{PC} = 2.5 Hz, 2-Me*C*$_6$H$_3$), 125.4 (br, 2-Me*C*$_6$H$_4$), 125.5 (d, J_{PC} = 2.4 Hz, 2-Me*C*$_6$H$_4$), 133.1 (d J_{PC} = 2.5 Hz, 2-Me*C*$_6$H$_4$), 133.4 (t, J_{PC} = 2.5 Hz, 2-Me*C*$_6$H$_4$), 137.7 (dd, J_{PC} = 7.3, 2.4Hz, 2-Me*C*$_6$H$_3$), 138.4 (s, 2-Me*C*$_6$H$_3$), 138.5 (s, 2-Me*C*$_6$H$_3$), 164.4 (dd, J_{PC} = 24, 3 Hz, 2-Me*C*$_6$H$_3$), 167.4 (dd, J_{PC} = 29, 3 Hz, 2-Me*C*$_6$H$_3$), 189.8 ("t", J_{PC} = 10 Hz, 2-Me*C*$_6$H$_4$). ^{31}P{^{1}H} NMR (chloroform-*d*, 36.3 MHz): δ 22.9, 30.3 (AB quartet, J = 128 Hz). Conductivity: Λ_M = 110 Ω^{-1} cm^2 mol^{-1}.

[Re(η^2-2-MeC$_6$H$_3$)(2-MeC$_6$H$_4$)$_2$(PMe$_3$)$_2$][BPh$_4$] ([2a][BPh$_4$]). Compound [**2a**][PF$_6$] (0.10 g, 0.13 mmol) and NaBPh$_4$ (0.2 g, excess) were stirred for 8 h in THF (10 cm^3). 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. ^{1}H NMR (dichloromethane-*d*$_2$, 250 MHz): δ 0.46 (s, 6 H, 2-*Me*C$_6$H$_4$), 1.68 ("d", J = 10 Hz, 18 H, PMe$_3$), 2.95 (s, 3 H, 2-*Me*C$_6$H$_3$), 6.57 (d, J = 9 Hz, 2 H), 6.75 (t, J = 7 Hz, 2 H), 6.86 (t, J = 7Hz, 4 H), 7.01 (t, J = 8 Hz, 8 H), 7.18 (d, 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, 1H), 7.78 (t, J = 8 Hz, 1 H), 8.29 (d, J = 7 Hz, 1 H). ^{31}P{^{1}H} NMR (dichloromethane-*d*$_2$, 36.3 MHz): δ 18.8, 25.7 (AB quartet, J = 134 Hz).

[Re(η^2-2-MeC$_6$H$_3$)(2-MeC$_6$H$_4$)$_2$(PMe$_3$)$_2$][OTf] ([2a][OTf]). HOTf (0.014 cm^3, 0.32 mmol) was added to a diethyl ether solution of **2a** (0.10 g, 0.16 mmol in 10 cm^3). 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 C$_{28}$H$_{38}$F$_3$P$_2$O$_3$ReS: 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. ^{1}H 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). ^{31}P{^{1}H} NMR (chloroform-*d*, 36.3 MHz): δ 17.3, 25.0 (AB quartet, J = 131 Hz).

[Re(η^2-2-MeC$_6$H$_3$)(2-MeC$_6$H$_4$)$_2$(PMe$_3$)$_2$][I$_5$] ([2a][I$_5$]). Excess iodine (ca. 100 mg) was added to a THF solution (10 cm^3) of **2a** (0.06 g, 0.1 mmol). The orange solution was evaporated in vacuo; the residue was extracted into dichloromethane (10 cm^3) and the solution filtered. After concentration to ca. 3 cm^3, diethyl ether was added (5 cm^3) 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$_4$P$_2$Re: 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. ^{1}H 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). ^{31}P{^{1}H} NMR (chloroform-*d*, 36.3 MHz): δ 17.4, 24.5 (AB quartet, J = 133 Hz).

[Re(η^2-2-MeC$_6$H$_3$)(2-MeC$_6$H$_4$)$_2$(PMe$_2$Ph)$_2$][PF$_6$] ([2b][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 C$_{37}$H$_{42}$F$_6$P$_3$Re: 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. ^{1}H NMR (chloroform-*d*, 250 MHz): δ 0.56 (s, 6 H, 2-*Me*C$_6$H$_4$), 1.99 (d, J_{PH} = 9 Hz, 6 H, P*Me*$_2$Ph), 2.04 (d, J_{PH} = 9 Hz, 6 H, P*Me*$_2$Ph), 2.59 (s, 3 H, 2-*Me*C$_6$H$_3$), 5.98 (d, J = 7 Hz, 2 H, PMe$_2$*Ph*), 6.68 (t, J = 8 Hz, 2 H, PMe$_2$*Ph*), 6.85 ("q", J = 7 Hz, 4 H, 2-MeC$_6$*H*$_4$), 7.11 (t, J = 7 Hz, 2 H, PMe$_2$*Ph*), 7.27 (m, 6 H), 7.44 (m, 2 H, 2-MeC$_6$*H*$_4$), 7.56 (d, J = 7 Hz, 1 H, 2-MeC$_6$*H*$_3$), 7.79 (t, J = 7 Hz, 1 H, 2-MeC$_6$*H*$_3$), 8.36 (d, J = 7 Hz, 1 H, 2-MeC$_6$*H*$_3$). ^{13}C{^{1}H} NMR (chloroform-*d*, 69.7 MHz): 14.45 (d, J_{PH} = 35 Hz, P*Me*$_2$Ph), 15.74 (d, J_{PC} = 34 Hz, P*Me*$_2$Ph), 23.14 (s, 2-*Me*C$_6$H$_3$), 26.63 (s, 2-*Me*C$_6$H$_4$), 124–138 (2-Me*C*$_6$H$_3$, 2-Me*C*$_6$H$_4$, PMe$_2$*Ph*), 163.8 (br d, J = 28 Hz, 2-Me*C*$_6$H$_3$), 167.6 (br d, J = 30 Hz, 2-Me*C*$_6$H$_3$), 189.2 ("t", J = 10 Hz, 2-Me*C*$_6$H$_4$). ^{31}P{^{1}H} NMR (chloroform-*d*, 36.3 MHz): δ 20.7, 25.4 (AB quartet, J = 133 Hz).

[Re(η^2-2-MeC$_6$H$_3$)(2-MeC$_6$H$_4$)$_2$(PMe$_2$Ph)$_2$][OTf] ([2b][OTf]). (a) From 2b + Me$_3$SiOTf. A solution of **2b** (0.10 g, 0.14 mmol) and Me$_3$SiOTf (0.026 cm^3, 0.14 mmol) was warmed to 40 °C for 2 h in THF (10 cm^3). Addition of hexane (50 cm^3) 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 C$_{38}$H$_{42}$F$_3$O$_3$P$_2$ReS: 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}H NMR (chloroform-*d*, 270 MHz): δ 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). ^{31}P{^{1}H} NMR (chloroform-*d*, 36.3 MHz): δ 18.0, 23.6 (AB quartet, J = 133 Hz). Conductivity: Λ_M = 103 Ω^{-1} cm^2 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-MeC$_6$H$_3$)(2-MeC$_6$H$_4$)$_2$(PMe$_2$Ph)$_2$][Co(CO)$_4$] ([2b][Co(CO)$_4$]). A hexane solution of Co$_2$(CO)$_8$ (0.047 g, 0.14 mmol in 20 cm^3) was added to a hexane solution of **2b** (0.10 g, 0.14 mmol in 10 cm^3). 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 C$_{41}$H$_{42}$CoP$_2$O$_4$Re: 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} cm^2 mol^{-1}.

Reaction of [2b][PF$_6$] with LiBEt$_3$H. A THF solution (10 cm^3) of [**2b**][PF$_6$] (0.10 g, 0.11 mmol) and LiBEt$_3$H (0.11 cm^3 of a 1 M solution in THF) was stirred overnight. After evaporation and extraction into hexane (20 cm^3), the red filtrate was concentrated to ca. 2 cm^3 and cooled (–15 °C) to give 0.06 g (74%) of dark red crystalline **2b** (by IR and mp).

Reaction of [2b][PF$_6$] with Me$_3$SiCH$_2$MgCl. A solution of Me$_3$SiCH$_2$MgCl in THF (0.085 cm^3 of a 1.2 M solution) was added to [**2b**][PF$_6$] (0.09 g, 0.1 mmol) in THF (10 cm^3). 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][I_5]

	x	*y*	*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 × 0.30 × 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 Kα radiation (λ = 0.71069 Å) and refined by using setting angles for 25 well-spaced reflections with $9.7 \le \theta \le 17.4°$. 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 Å^3, M_r 1246.22 Z = 4, D_{calcd} = 2.23 g cm^{-3}, μ = 73.0 cm^{-1}, $F(000)$ = 2284 at T = 291 K.

Intensity data were recorded by using the $\omega/2\theta$ scan technique with $1.5 \le \theta \le 25°$, $h = 0 \rightarrow 22$, $k = 0 \rightarrow 16$, $l = 0 \rightarrow 16$, 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 = $[\sigma^2(F_o) + 0.0002F_o^2]^{-1}$. 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**][PF_6], 117407-53-1; [**2a**][BPh_4], 117467-85-3; [**2a**][OTf], 117467-86-4; [**2a**][I_5], 117467-87-5; **2b**, 117407-51-9; [**2b**][PF_6], 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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[14] Sheldrick, G. M. SHELXS 86, Program for crystal structure determination; University of Göttingen: Göttingen, FDR, 1986.

[15] Sheldrick, G. M. SHELX 76, Program for crystal structure calculations; University of Cambridge: Cambridge, England, 1976.

Deprotonation and Anionic Rearrangement in CpRe(NO)(R)(PPh$_3$) (R = CHO, CH$_3$)

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The mechanism of migration of the CHO ligand from the metal to the deprotonated cyclopentadienyl ring in $[(\eta^5\text{-}C_5H_4)Re(NO)(CHO)(PPh_3)]^-$ 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$_6$H$_5$, C(O)CH$_2$C$_6$H$_5$, C(O)H, H, CH$_3$CHCN, (CH$_3$)$_2$CH, H$_2$CH, H$_2$CC$_6$H$_5$, and H$_2$CCH=CH$_2$.[1-6] Some

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