An Isolable Organometallic Cation Radical in Which a C_4 Chain Conducts Charge between Two Chiral and Configurationally Stable Rhenium Termini

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Summary: The deep green, chiral, configurationally stable cation radical (SS,RR)-$[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(CCCC)(Ph_3P)(ON)Re(\eta^5\text{-}C_5Me_5)]^{\bullet+}PF_6^-$ is prepared by comproportionation of the corresponding neutral and dicationic C_4 complexes or $Ag^+PF_6^-$ oxidation of the neutral complex (50–69%). ESR and IR data indicate complete spin delocalization between the two rheniums, and UV/visible/near-IR absorptions are described.

Compounds in which linear unsaturated chains of elemental carbon span two transition metals, $L_nMC_xM'L'_{n'}$, are now available for $x = 1$–4.[1,2] As x becomes larger, possible analogies with polyacetylenes become apparent.[3,4] In particular, charge density in oxidized or reduced states might be efficiently delocalized along the MC_xM assembly, which may in turn lead to useful bulk attributes. This, together with exciting recent advances in metallaradical bond activation and catalysis,[5] and other unique properties of paramagnetic organometallic compounds,[6] prompted us to seek isolable, odd valence electron C_x complexes.

In a predecessor effort,[1c] the diamagnetic neutral and dicationic ReC_4Re complexes (*SS,RR*)-$(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CC{\equiv}C)(Ph_3P)(ON)Re(\eta^5\text{-}C_5Me_5)$ ((*SS,RR*)-**2**) and (*SS,RR*)-$[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)({=}C{=}C{=}C{=}C{=})(Ph_3P)(ON)Re(\eta^5\text{-}C_5Me_5)]^{2+}(PF_6^-)_2$ ((*SS,RR*)-$\mathbf{2}^{2+}(PF_6^-)_2$) were isolated and structurally characterized (Scheme I). The rhenium atoms have 18 valence electron, d^6 configurations, and are 7.83–7.63 Å apart. A cyclic voltammogram of the former was recorded under the conditions described in Figure 1. Two chemically reversible one electron oxidations occurred at +0.06 and +0.50 V (ΔE_p 60 mV).[7] Thus, the intermediate cation radical, (*SS,RR*)-$\mathbf{2}^{\bullet+}X^-$, was viewed as a viable synthetic target.

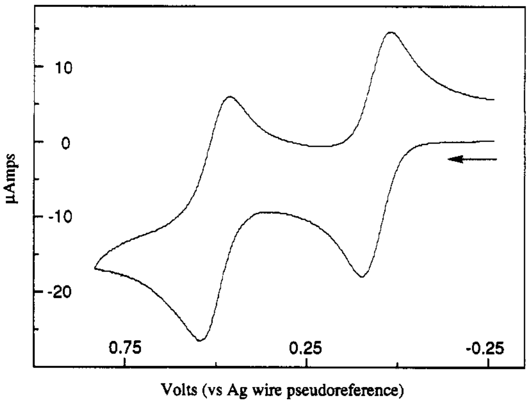
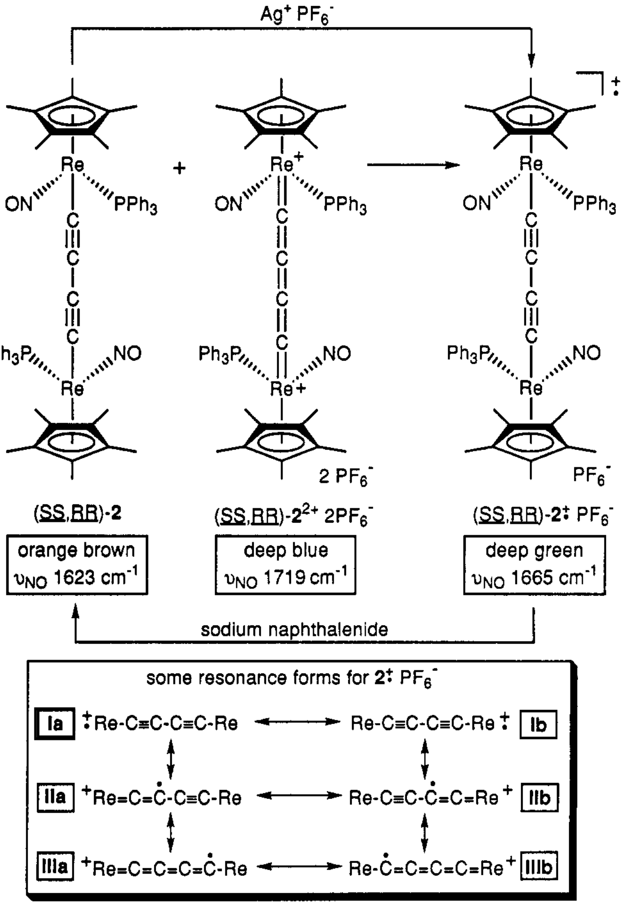


Figure 1. Cyclic voltammogram of (*SS,RR*)-**2** (3×10^{-3} M in 0.1 M $Et_4N^+ClO_4^-/CH_3CN$; $E^{\circ\prime}$(ferrocene) = 0.56 V; scan rate = 100 mV/s).

Scheme I. Synthesis of a Paramagnetic ReC_4Re Complex



From the emf of the half-reactions, a large K_{eq} (2.9×10^7) was calculated for the *com*proportionation of (*SS,RR*)-**2** and (*SS,RR*)-$\mathbf{2}^{2+}(X^-)_2$ to (*SS,RR*)-$\mathbf{2}^{\bullet+}X^-$ (Scheme

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[1] Lead references for $x = 4$: (a) Rappert, T.; Nürnberg, O.; Werner, H. *Organometallics* **1993,** *12,* 1359. (b) Le Narvor, N.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1993,** 357. (c) Zhou, Y.; Seyler, J. W.; Weng, W.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1993,** *115,* 8509. (d) See also Worth, G. H.; Robinson, B. H.; Simpson, J. *Organometallics* **1992,** *11,* 3863. Osella, D.; Gambino, O.; Nevi, C.; Ravera, M.; Bertolino, D. *Inorg. Chim. Acta* **1993,** *206,* 155.

[2] For lead references for $x = 1$–3, see earlier papers in this series: (a) Ramsden, J. A.; Weng, W.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1992,** *114,* 5890. (b) Weng, W.; Ramsden, J. A.; Arif, A. M.; Gladysz, J. A. *Ibid.* **1993,** *115,* 3824.

[3] (a) Tolbert, L. *Acc. Chem. Res.* **1992,** *25,* 561. (b) Bally, T.; Roth, K.; Tang, W.; Schrock, R. R.; Knoll, K.; Park, L. Y. *J. Am. Chem. Soc.* **1992,** *114,* 2440. (c) Jozefiak, T. H.; Ginsburg, E. J.; Gorman, C. B.; Grubbs, R. H.; Lewis, N. H. *Ibid.* **1993,** *115,* 4705.

[4] A more precise comparison would be to a polymeric chain of sp-hybridized carbons. However, this material, termed "carbyne" or "chaoite", remains poorly characterized. See: Diederich, F.; Rubin, Y. *Angew. Chem., Int. Ed. Engl.* **1992,** *31,* 1101 and references therein.

[5] (a) Wayland, B. B.; Ba, S.; Sherry, A. E. *J. Am. Chem. Soc.* **1991,** *113,* 5305 and references therein. (b) Togni, A.; Rist, G.; Rihs, G.; Schweiger, A. *Ibid.* **1993,** *115,* 1908.

[6] (a) Baird, M. C. *Chem. Rev.* **1988,** *88,* 1217. (b) Astruc, D. *Acc. Chem. Res.* **1991,** *24,* 36. (c) Tyler, D. R. *Ibid.* **1991,** *24,* 325.

[7] The *SS,RR* diastereomer and samples enriched in the *SR,RS* diastereomer gave identical data.

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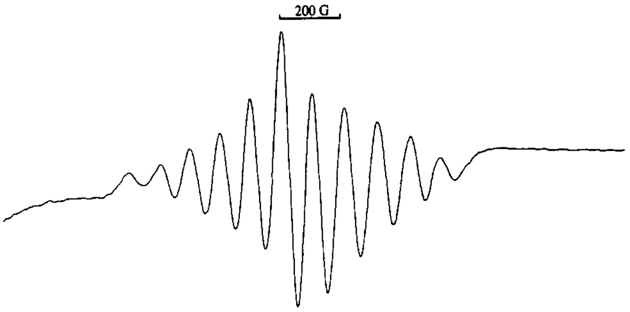

Figure 2. ESR spectrum of (*SS,RR*)-**2**$^{\bullet+}$PF$_6^-$ (CH_2Cl_2, ambient temperature, 7.0×10^{-3} M).

I). Hence, (*SS,RR*)-**2** (1.1 equiv) and (*SS,RR*)-**2**$^{2+}$(PF$_6^-$)$_2$ were combined in CH_2Cl_2. Workup gave (*SS,RR*)-**2**$^{\bullet+}$PF$_6^-$ as a deep green, analytically pure powder in 50% yield.[8,9] Reaction of (*SS,RR*)-**2** and Ag$^+$PF$_6^-$ (1.0 equiv) in toluene also gave (*SS,RR*)-**2**$^{\bullet+}$PF$_6^-$ (69%). Solid (*SS,RR*)-**2**$^{\bullet+}$PF$_6^-$ was stable for weeks under an inert atmosphere, but some decomposition was evident after several hours in degassed CH_2Cl_2 or CH_3CN. Diastereomeric purity was assayed as described below. The magnetic susceptibility indicated one unpaired electron (2.1 μ_B, Evans NMR and balance methods). Samples enriched in the opposite diastereomer (*SR,RS*)-**2**$^{\bullet+}$PF$_6^-$, and with ^{13}C labeled bridges, were similarly prepared.

We sought to probe the electronic structure of (*SS,RR*)-**2**$^{\bullet+}$PF$_6^-$, for which many resonance forms are possible (**I–III**, Scheme I). First, IR spectra showed a single ν_{NO} absorption in both solution and the solid state (cm^{-1}, CH_2Cl_2/KBr 1665/1654 (s)).[7] The band was between those of (*SS,RR*)-**2** and (*SS,RR*)-**2**$^{2+}$(PF$_6^-$)$_2$ (1623, 1719; CH_2Cl_2), indicating intermediate metal-to-ligand back-bonding. The $\nu_{C\equiv C}$ value, 1872/1870 (m), was lower than that of (*SS,RR*)-**2** (1964 w) and shifted to 1799 in the $^{13}C_4$ analog (calcd 1799).

An ESR spectrum (Figure 2) showed a simple undecet with broad individual lines (*g* 2.02; $A_{iso,Re}$ 98 G; ΔH_{pp} 49 G).[7] Since rhenium has two principal isotopes, each with I = $^5/_2$ (^{185}Re 37.05%, ^{187}Re 62.93%), a superposition of a sextet of sextets (^{185}Re/^{187}Re) with two undecets (^{185}Re/^{185}Re, ^{187}Re/^{187}Re) might have been expected. However, the ^{185}Re and ^{187}Re magnetic moments differ by only 1%. Thus, the three isotopomers give essentially identical spectra.[10] Surprisingly, ESR data are available for only a few other rhenium-centered radicals.[8a,e] $A_{iso,Re}$ values of 190 and 156 G can be calculated for two isomeric $^\bullet$Re(CO)$_3$(PCy$_3$)$_2$ species.[8a] Significantly, these are approximately twice that of the dirhenium radical (*SS,RR*)-**2**$^{\bullet+}$PF$_6^-$.

These data establish that the odd electron in (*SS,RR*)-**2**$^{\bullet+}$PF$_6^-$ is fully delocalized between the two rheniums, at least on the very rapid IR and ESR time scales (10^{-13}–10^{-9} s). An 18/17 valence electron or d^6/d^5 ground state (**Ia** or **Ib**) should give two IR ν_{NO} bands and much different ESR spectra. Also, there is extensive literature on d^6/d^5 mixed valence complexes with varying degrees of electronic delocalization and distinguishing optical properties.[11] Thus, UV/visible/near-IR spectra were recorded (Figures 3 and 4). Complex (*SS,RR*)-**2** showed an absorption at 350 nm (ϵ 16 900 M^{-1} cm^{-1}), and (*SS,RR*)-**2**$^{2+}\cdot$2PF$_6^-$ gave bands at 390 and 578 nm (ϵ 39 600, 28 100). Complex (*SS,RR*)-**2**$^{\bullet+}$PF$_6^-$ gave absorptions at 348 and 454 nm (ϵ 24 000, 6400), and unique near-IR bands at 883, 1000, and 1200 nm (ϵ 15 000, 9400 (sh), 3200).[7] Although further study of these transitions is merited, localized d^6/d^5 complexes generally give a single, weaker, near-IR absorption ($\epsilon \leq 1000$; "intervalence transfer").[11] Interestingly, cation radicals formed from polyacetylene oligomers R—(CH=CH)$_n$—R also give multiple near-IR bands.[3b]

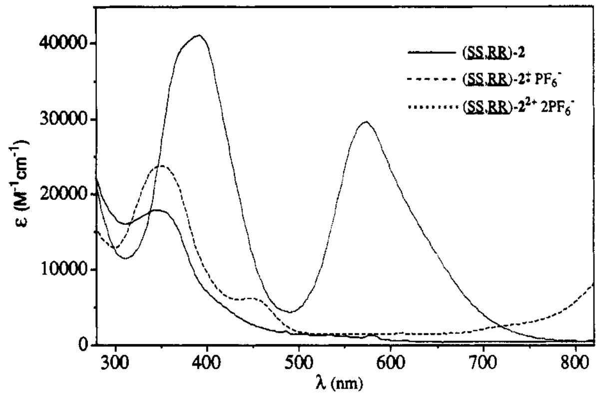

Figure 3. UV/visible spectra of (*SS,RR*)-**2**, (*SS,RR*)-**2**$^{\bullet+}$PF$_6^-$ and (*SS,RR*)-**2**$^{2+}$(PF$_6^-$)$_2$ (CH_2Cl_2, ambient temperature, (1.7–2.9) $\times 10^{-5}$ M).

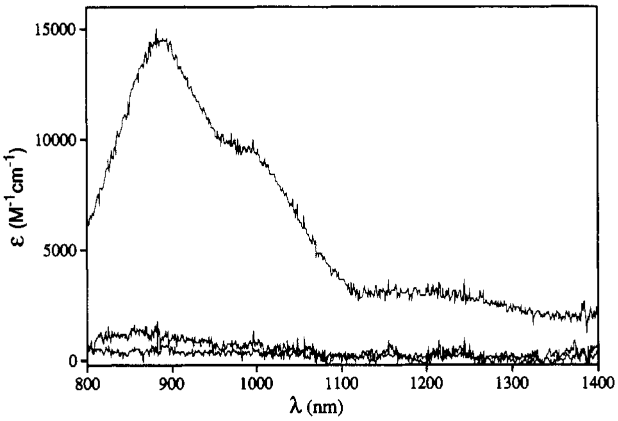

Figure 4. Near-IR spectrum of (*SS,RR*)-**2**$^{\bullet+}$PF$_6$ (CH_2Cl_2, ambient temperature, 1.7×10^{-5} M). Background spectra of (*SS,RR*)-**2** and (*SS,RR*)-**2**$^{2+}$(PF$_6^-$)$_2$ are given for comparison.

To our knowledge, (*SS,RR*)-**2**$^{\bullet+}$PF$_6^-$ is the only mixed valence-type complex in which both metals are stereocenters. Thus, configurational stability can be probed.[12] First, CH_2Cl_2 solutions of (*SS,RR*)-**2**$^{\bullet+}$PF$_6^-$ and samples enriched in (*SR,RS*)-**2**$^{\bullet+}$PF$_6^-$ were stirred for 4 h in the dark. Then sodium naphthalenide was added. Workup gave **2** in 72% yield. NMR analyses (^{1}H, ^{31}P) showed diastereomer ratios that were identical with those of the samples of **2** originally used to prepare **2**$^{\bullet+}$PF$_6^-$. Hence,

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(8) For other isolable paramagnetic rhenium compounds, see: (a) Walker, H. W.; Rattinger, G. B.; Belford, R. L.; Brown, T. L. *Organometallics* **1983**, *2*, 775. (b) Crocker, L. S.; Heinekey, D. M.; Schulte, G. K. *J. Am. Chem. Soc.* **1989**, *111*, 405. (c) Detty, M. R.; Jones, W. D. *Ibid.* **1987**, *109*, 5666. (d) deLearie, L. A.; Pierpont, C. G. *Ibid.* **1987**, *109*, 7031. (e) deLearie, L. A.; Haltiwanger, R. C.; Pierpont, C. G. *Inorg. Chem.* **1987**, *26*, 817.

(9) For structurally characterized (η^5-C$_5$H$_5$)Cr(NO)(PPh$_3$)(R)$^\bullet$ and alkynyl iron radicals, see: (a) Herring, F. G.; Legzdins, P.; McNeil, W. S.; Shaw, M. J. *J. Am. Chem. Soc.* **1991**, *113*, 7049. (b) Bianchini, C.; Laschi, F.; Masi, D.; Ottaviani, F. M.; Pastor, A.; Peruzzini, M.; Zanello, P.; Zanobini, F. *Ibid.* **1993**, *115*, 2723.

(10) ESR spectra recorded at 77 K, or of the $^{13}C_4$ analog, did not show additional couplings. However, the IR $\nu_{C\equiv C}$ value suggests a reduced C≡C bond order and resonance contributions by **II** or **III** (Scheme I).

(11) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1.

(12) Iron cation radicals [(η^5-C$_5$H$_5$)Fe(CO)(L)(CH$_3$)]$^{\bullet+}$ rapidly lose configuration: Brunner, H.; Fisch, K.; Jones, P. G.; Salbeck, J. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1521.

2$^{\bullet +}$PF$_6^-$ does not readily epimerize in solution, and configuration must be retained for all reactions in Scheme I.

During the course of our study, Lapinte reported a related FeC$_4$Fe cation radical, [(η^5-C$_5$Me$_5$)Fe(dppe)-(C≡CC≡C)(dppe)Fe(η^5-C$_5$Me$_5$)]$^{\bullet +}$PF$_6^-$.[1b] Based upon IR and Mössbauer data, he likewise assigns a delocalized ground state. Also, the Co$_3$C$_4$Co$_3$ complex (CO)$_9$Co$_3$-CC≡CCCo$_3$(CO)$_9$ undergoes two chemically reversible one electron reductions.[1d] However, (*SS,RR*)-**2** is not reduced at the cathodic limit of Figure 1 (−0.7 V). In summary, the unsaturated ReC$_4$Re linkage in (*SS,RR*)-**2**$^{\bullet +}$PF$_6^-$ allows electron delocalization onto any of six atoms over a ca. 7.7-Å span (**I**–**III**). This wirelike chiral assembly should be easily accessed in enantiomerically pure form, and with higher carbon chains. These themes, and the reactivities of the ReC$_4$Re compounds as a function of oxidation state, will be the focus of future reports.[13]

Supplementary Material Available: Textual description of key experimental details (3 pages). Ordering information is given on any current masthead page.

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[13] We thank the NSF for support of this research.