Propionic acid-*d* (65 mL) was added and the mixture was slowly heated to 150 °C. After 5 h, fractions with bp <145 °C were collected and washed with 10% $NaHCO_3$ and with H_2O. The crude product was dried over $MgSO_4$ and fractionally distilled to give 13.0 g (39.5%) of the title compound with bp 94 °C/680 Torr. GC-MS analysis showed 90.5% deuterium incorporation.

5(6)-Deuterio-*exo*-2-bicyclo[2.2.1]heptyl Tosylate (6). The 5(6)-deuteriobicyclo[2.2.1]hept-2-ene was hydroborated and oxidized with H_2O_2 according to Brown's procedure.[24] The crude alcohol was reacted with tosyl chloride in pyridine[22b] to give a 37.5% yield (overall from the alkene) of **6**, mp 35.5 °C.

***exo*-3-Deuterio-*exo*-2-chlorobicyclo[2.2.1]heptane (5).** To 21.3 g (0.25 mol) of freshly distilled pyridine in 80 mL of cold water were added 20.2 (0.25 mol) of concentrated HCl and 200 mL of Et_2O. The mixture was cooled to 5 °C and Chlorox (445 g, 0.31 mol of sodium hypochlorite) was added at such a rate that the temperature did not exceed 15 °C. After stirring for 1 h at room temp, the layers were separated, and the aqueous layer was extracted with Et_2O (2 × 100 mL). The combined Et_2O layers were washed with 25 mL of 8% H_2SO_4 and 25 mL of 5% NaOH before being dried over $CaCl_2$.

Bicyclo[2.2.1]hept-2-ene (19.8 g, 0.21 mol) was deuteroborated[24] with externally generated B_2D_6 (from $NaBD_4$ and $BF_3{\cdot}Et_2O$) in 350 mL of Et_2O. The slight excess of B_2D_6 was destroyed by adding a small amount of H_2O. To the reaction mixture was added 25 mL of piperidine followed by the *N*-chloropiperidine in Et_2O solution prepared above. The resulting solution was stirred at room temperature for 4 days under nitrogen and poured into a separatory funnel partially filled with crushed ice. HCl (9 N, 100 mL) was added and the mixture was extracted with Et_2O. Sodium bisulfite solution (38 g in 100 mL of H_2O) was added to destroy the excess *N*-chloropipiridine and the Et_2O layer was separated and washed with 0.2 N HCl (2 × 250 mL) and once with dilute aqueous Na_2CO_3. After drying over Na_2SO_4, the solution was concentrated at atmorpheric pressure. The residual liquid was distilled under vacuum to give 7.4 g (27%) of **5** as the main fraction, bp 66.5–67 °C/15 Torr (lit.[25] bp 84–88 °C/76 Torr). ^1H NMR ($CDCl_3$): δ 1.0–2.0 (m, 7 H), 2.40 (s, 2 H), 3.93 (d, J = 7.2 Hz, 1 H).

***exo*-2-Chlorobicyclo[2.2.1]heptane (8).** Using the same procedure, 15.1 g (57%) of **8** with bp 66.5–67 °C/15 Torr was obtained from 18.8 g (0.20 mol) of bicyclo[2.2.1]hept-2-ene.

Acknowledgment. Support of this research by the donors of the Petroleum Research Fund, administered by the Americal Chemical Society, is gratefully acknowledged.

---

[24] Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1961**, *83*, 2544.

[25] Brown, H. C. *Hydroboration*; W. A. Benjamin, Inc.; New York, 1962; p 130.

[26] Kooijman, E. C.; Vegter, G. C. *Tetrahedron* **1958**, *4*, 382.

"Spin–Charge Exchange" in Allodial Radical Ions, a Novel Intramolecular Single Electron Transfer Equilibrium

Manuel Ballester,* Isabel Pascual, Juan Riera, and Juan Castañer

Departamento de Materiales Orgánicos Halogenados, Centro de Investigación y Desarrollo (CSIC), Jordi Girona, 18-24, 08034 Barcelona, Spain

Received March 15, 1990

The intramolecular single-electron transfer in radical anions and radical cations, constituted by two identical triphenylmethyl moieties, has been studied. The preparation of the radical ions has been effected by mixing the corresponding stable diions (tetra-*n*-butylammonium or hexachloroantimonate salts) and chemically inert diradicals: by partial oxidation of the dianion salts with iodine (radical anions) and by partial oxidation of the diradicals with $SbCl_5$ (radical cations). The ESR ^{13}C hyperfine coupling constants and linewidths and UV–vis absorptivity spectra afford compelling evidence for a rapid spin–charge exchange equilibrium:

$$(C_6Cl_5)_2\overset{\bullet}{C}\text{-}C_6Cl_4\text{-}Sp\text{-}C_6Cl_4\text{-}\overset{*}{C}(C_6Cl_5)_2 \rightleftharpoons (C_6Cl_5)_2\overset{*}{C}\text{-}C_6Cl_4\text{-}Sp\text{-}C_6Cl_4\text{-}\overset{\bullet}{C}(C_6Cl_5)_2$$

(Sp = none, CH_2CH_2, C≡C. * = –, +). Relevant structural aspects, such as steric inhibition of resonance, electron paths, and counterion involvement, are discussed. The synthesis and isolation of related disalts from the corresponding diradicals are also described.

Introduction

The trivalent carbon radicals of the perchlorotriphenylmethyl (PTM) series posses a chemical inertness and a thermal stability much greater than those of the overwhelming majority of tetravalent carbon compounds and materials.[1-3] In fact, their half-lives in solution, in the air, are of the order of 100 years, and they withstand harsh chemicals (H_2SO_4, HNO_3, NO, NO_2, Cl_2, Br_2, etc.) and temperatures up to 300 °C in the air. The unique inertness of such radicals is due to molecular overcrowding by their chlorine substituents which shield effectively their would be normal reaction sites.

Therefore, these inert free radicals (IFRs) are quite appropriate for the study of reactions involving radicals and nonradical species, as single-electron transfers between radicals and ions, particularly those between inert 4-X-tetradecachlorotriphenylmethyl radicals (X-PTM$^\bullet$) and low reactivity, stable 4-Y-tetradecachlorotriphenylmethyl anions (Y-PTM:$^-$). This process, which has recently been investigated (Scheme I),[4] leads to SET equilibria, the equilibration rates of which are unusually slow mainly

---

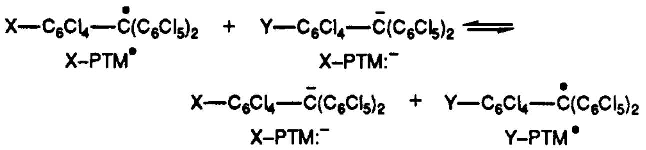
[1] Ballester, M.; Riera, J.; Castañer, J.; Badía, C.; Monsó, J. M. *J. Am. Chem. Soc.* **1971**, *93*, 2215. Monsó, J. M. Doctoral Thesis, University of Barcelona, 1969.

[2] Ballester, M. *Acc. Chem. Res.* **1985**, 380.

[3] Ballester, M. *Adv. Phys. Org. Chem.* **1989**, *25*, 267–445.

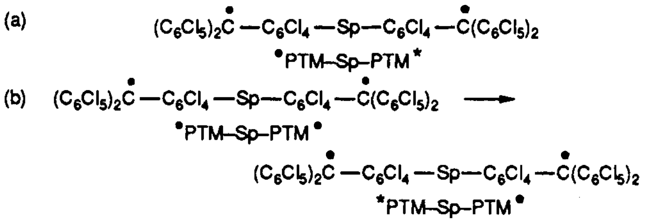
0022-3263/91/1956-0217$02.50/0 © 1991 American Chemical Society

Scheme I



$$\underset{X\text{-}PTM^{\bullet}}{X{-}C_6Cl_4{-}\overset{\bullet}{C}(C_6Cl_5)_2} + \underset{X\text{-}PTM{:}^-}{Y{-}C_6Cl_4{-}\bar{C}(C_6Cl_5)_2} \rightleftharpoons \underset{X\text{-}PTM{:}^-}{X{-}C_6Cl_4{-}\bar{C}(C_6Cl_5)_2} + \underset{Y\text{-}PTM^{\bullet}}{Y{-}C_6Cl_4{-}\overset{\bullet}{C}(C_6Cl_5)_2}$$

Scheme II



$$\text{(a)}\quad \underset{{}^{\bullet}PTM\text{-}Sp\text{-}PTM^{*}}{(C_6Cl_5)_2\overset{\bullet}{C}{-}C_6Cl_4{-}Sp{-}C_6Cl_4{-}\overset{\bullet}{C}(C_6Cl_5)_2}$$

$$\text{(b)}\quad \underset{{}^{\bullet}PTM\text{-}Sp\text{-}PTM^{\bullet}}{(C_6Cl_5)_2\overset{\bullet}{C}{-}C_6Cl_4{-}Sp{-}C_6Cl_4{-}\overset{\bullet}{C}(C_6Cl_5)_2} \longrightarrow \underset{{}^{*}PTM\text{-}Sp\text{-}PTM^{\bullet}}{(C_6Cl_5)_2\overset{\bullet}{C}{-}C_6Cl_4{-}Sp{-}C_6Cl_4{-}\overset{\bullet}{C}(C_6Cl_5)_2}$$

(Sp (spacer) = none, C≡C, CH_2CH_2; * = +, −)

because of steric shielding by chlorine in both reaction components. In fact, while the second-order rate constant between radical anions and neutral species is usually in the 10^7–10^{10} mol^{-1} L s^{-1} range,[5,6] that between 4*H*-tetradecachlorotriphenylmethyl radical and 4-aminotetradecachlorotriphenyl carbanion is about 8 mol^{-1} L s^{-1};[4] i.e., a rate decrease greater than 6 powers of 10. Therefore, at concentrations about 2×10^{-4} mol L^{-1}, at room temperature, its progress is measured in minutes.

Results and Discussion

Since preceding studies on (*feudal*[3,7]) intramolecular SETs had suffered much from substrate unstability and high reactivity, as well as structural uncertainty, and consequently they frequently required rather sophisticated, unusual, and even heroic techniques (photoexitation in glasses, high-energy pulse radiolysis, high-vacuum techniques, etc.), as well as supporting hypotheses, it was particularly enticing to undertake a study on *intramolecular* SETs in *allodial*[3,7] radical carbanions, •PTM-Sp-PTM:$^-$, and radical carbenium ions, •PTM-Sp-PTM$^+$ (Scheme IIa), provided with both the chemical stability of the X-PTM• radicals[4] and the low reactivity of their carbanions (X-PTM:$^-$),[4] or carbenium ions (X-PTM$^+$).[8,9] For this purpose, the preparation of three bistriphenylmethyl diradicals and the syntheses of their diions have been effected (Scheme IIb). The diradicals are perchloro-$\alpha,\alpha,\alpha',\alpha'$-tetraphenylbi-*p*-tolyl-α,α'-diyl (•PTM-PTM•),[1] 1,2-ethylenebis(4-tetradecachlorotriphenylmethyl) (•PTM-CH_2CH_2-PTM•),[10] perchloroethynylenebis(4-triphenylmethyl) (•PTM-C≡C-PTM•).[11] It is pointed out that the UV–vis spectra of the two first diradicals is almost coincident with that of monoradical PTM• (Figure 1a), showing that in the relevant energy scale the electronic interaction between their two molecular moieties is almost nonexistent. The UV–vis spectrum of the third diradical evidences the presence of a π–π electronic interaction between each moiety and the triple bond (Figure 1b).

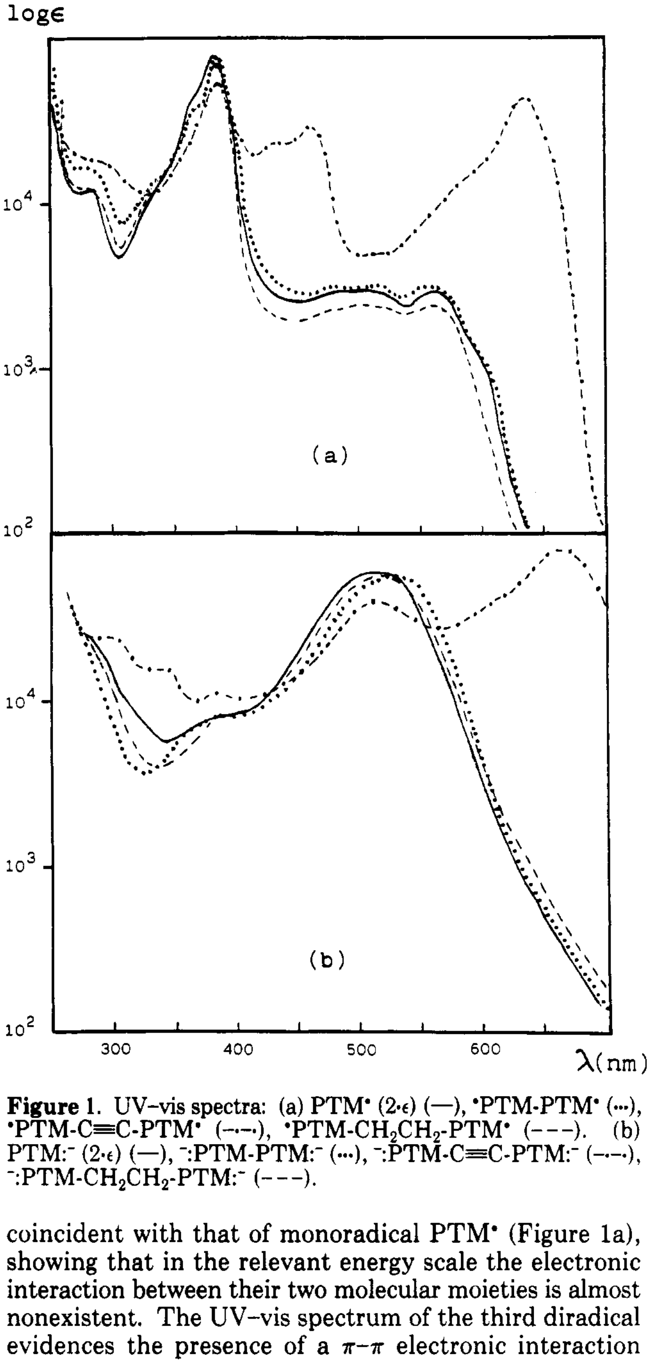


Figure 1. UV–vis spectra: (a) PTM• (2·ε) (—), •PTM-PTM• (···), •PTM-C≡C-PTM• (–·–·), •PTM-CH_2CH_2-PTM• (– – –). (b) PTM:$^-$ (2·ε) (—), $^-$:PTM-PTM:$^-$ (···), $^-$:PTM-C≡C-PTM:$^-$ (–·–·), $^-$:PTM-CH_2CH_2-PTM:$^-$ (– – –).

Perchloro-$\alpha,\alpha,\alpha',\alpha'$-tetraphenylbi-*p*-tolyl-α,α'-diyl dianion ($^-$:PTM-PTM:$^-$) tetra-*n*-butylammonium salt has been synthesized from either *H*PTM-PTM*H*[1] or from •PTM-PTM•[1] by reaction with hydroxide ion ((*n*-Bu)$_4$N$^+$ HO$^-$, in THF) (Scheme III). It is pointed out that this conversion from that diradical consists of two consecutive single-electron transfers where HO$^-$ *acts as an electron donor*.[2-4,12] The syntheses of tetra-*n*-butylammonium

Scheme III

$$^{\bullet}PTM\text{-}Sp\text{-}PTM^{\bullet} \xrightarrow{HO^-\ (a)} {}^{-}{:}PTM\text{-}Sp\text{-}PTM{:}^{-} \xleftarrow{HO^-\ (b)} HPTM\text{-}Sp\text{-}PTMH$$

(a) Sp = none, C≡C, CH_2CH_2; (b) Sp = none.

---

[4] Ballester, M.; Pascual, I.; Torres, J. *J. Org. Chem.* **1990**, *55*, 3035.

[5] Kochi, J. K. *Free Radicals*; Wiley-Interscience: 1973; Vol. 1, p 517.

[6] Szwarc, M. *Carbanions, Living Polymers and Electron Transfer Processes*; Interscience: New York, 1968; p 378.

[7] The terms "allodial" and "feudal", from Old German "äl-ôd" and "fëhu", respectively, have long been used by the authors and co-workers to designate two types of radical ions.[3] Allodial radical ion denotes that its electric charge and odd electron have an independent existence, such as in the radical ions dealt with here, while feudal radical ion is just the opposite: the electric charge arises from an electrically neutral, nonradical species by a single-electron addition or removal (ketyl radical anions, aromatic radical ions, cyclophane radical anions).

[8] Ballester, M.; Riera-Figueras, J.; Rodríguez-Siurana, A. *Tetrahedron Lett.* **1970**, 3615.

[9] Ballester, M.; Riera, J.; Castañer, J.; Rodríguez, A.; Rovira, C.; Veciana, J. *J. Org. Chem.* **1982**, *47*, 4498.

[10] Ballester, M.; Veciana, J.; Riera, J.; Castañer, J.; Rovira, C.; Armet, O. *J. Org. Chem.* **1986**, *51*, 2472.

[11] (a) Ballester, M.; Castañer, J.; Riera, J.; Ibáñez, A. *Tetrahedron Lett.* **1980**, *21*, 2435. (b) Ibáñez, A. Doctoral Thesis, University of Barcelona, 1972.

[12] Ballester, M. *Alkaromatic Chlorocarbons, Proc. OAR Res. Appls. Conf., USAF* **1967**, *1*, 242.

perchloroethynylenebis-4-triphenylmethide ($2(n\text{-Bu})_4\text{N}^{+-}$:PTM-C≡C-PTM:$^-$) and tetra-*n*-butylammonium 1,2-ethylenebis(4-tetradecachlorotriphenylmethide) ($2(n\text{-Bu})_4\text{N}^{+-}$:PTM-$\text{CH}_2\text{CH}_2$-PTM:$^-$) have been effected likewise from the corresponding diradicals. Their yields were good to excellent, and their identification has been effected by C, H, N, and Cl elemental analyses and IR and UV–vis spectra. Dianions $^-$:PTM-PTM:$^-$ and $^-$:PTM-CH_2CH_2-PTM:$^-$ display absorption maxima at 525 nm (ϵ 59500) and 517 (56700), respectively (Figure 1b). The absorption maxima of dianion $^-$:PTM-C≡C-PTM:$^-$ are located at 515 nm (ϵ 40000) and 665 (82500) (Figure 1b). The presence of the latter band suggests π–π interaction, as in the corresponding diradical. The $^-$:PTM-C≡C-PTM:$^-$ salt decomposes in THF solution, at room temperature (hours), to a compound displaying a very intense band at 750 nm, suggesting a cyclization reaction leading to an increased π–π conjugation. In this connection it is emphasized that both $^-$:PTM-PTM:$^-$ and $^-$:PTM-CH_2CH_2-PTM:$^-$ absorption maxima are almost coincident with that of PTM:$^-$ (525 nm ($\epsilon/2$ 30000) vs. 513 (33800);[4] Figure 1b) and Me-PTM:$^-$ (517 nm ($\epsilon/2$ 28250) vs. 517 (27200)[4]), respectively. This indicates that electronic interaction between their moieties is insignificant. These dicarbanions salts are stable, although a very slow oxidation to their diradicals may take place.

Osmometric measurements have been performed on $2(n\text{-Bu})_4\text{N}^+$ $^-$:PTM-PTM:$^-$ in THF (7.5×10^{-3} mol L^{-1}), the resulting mean molecular weight being 1160. This indicates that that salt is mainly in the form of ion pairs [$(n\text{-Bu})_4\text{N}^+$ $^-$:PTM-PTM:$^-$] and free $(n\text{-Bu})_4\text{N}^+$ ions, the ratio of [$(n\text{-Bu})_4\text{N}^+$ $^-$:PTM-PTM:$^-$]/[$2(n\text{-Bu})_4\text{N}^+$ $^-$:PTM-PTM:$^-$] being 2.0.

Since in solution the salts $(n\text{-Bu})_4\text{N}^+$ X-PTM:$^-$ exist overwhelmingly as ion pairs,[4] that unexpected result suggests that the positive charges of the two counterions are closer to the center of the dicarbanion molecule than its two negative charges, and consequently, electrostatic repulsion assists its ionic dissociation (Scheme IV).

Scheme IV

$$2(n\text{-Bu})_4\text{N}^+\ ^-\text{:PTM-PTM:}^- \rightleftharpoons (n\text{-Bu})_4\text{N}^+ + [(n\text{-Bu})_4\text{N}^+\ ^-\text{:PTM-PTM:}^-]$$

Dicarbenium Ion $^+$PTM-PTM$^+$. The synthesis of $^+$PTM-PTM$^+$ by oxidation of diradical $^•$PTM-PTM$^•$ has been realized with SbCl_5 in SO_2Cl_2, as that of PTM$^+$ SbCl_6^- from radical PTM$^•$.[8,9] Nevertheless, additional information on the latter process has been required in order to undertake it properly.

The oxidation of PTM$^•$ with SbCl_5 had been performed in an excellent yield,[8,9] its stoichiometry being that shown in Scheme Va. This cationization has been repeated but using CH_2Cl_2 as the solvent. The final reaction composition has been ascertained by hydrolytic quenching, giving a mixture of unreacted radical PTM$^•$ and perchlorofuchsone I (Scheme Vb), the latter resulting from PTM$^+$.[8,9] Even employing a substantial molar excess of SbCl_5 the yield in PTM$^+$ is less than 50% of theory, suggesting that an equilibrium is established. Accordingly, it has been found that by adding SbCl_3 to a solution of PTM$^+$ SbCl_6^-, in CH_2Cl_2, a 65% yield of radical PTM$^•$ is obtained, the yield increasing up to 92% in the absence of solvent. When to about an equimolecular mixture of PTM$^•$ and SbCl_5, in CH_2Cl_2, Cl_2 is added, the yield of cation PTM$^+$ increases significantly (from less than 45 to 69%), this being due to the conversion of SbCl_3 into SbCl_5 (Scheme Vc), i.e., the equilibrium of Scheme Va is then being shifted to its right-hand side. It has also been found that conversion to PTM$^+$ can also be effected by substituting SbCl_5 by a mixture of SbCl_3 and excess of Cl_2 (82%). Therefore, this is a reversible redox system.

Scheme V

$$\text{(a) } 2\text{PTM}^• + 3\text{SbCl}_5 \rightleftharpoons 2\text{PTM}^+ + \text{SbCl}_3 + 2\text{SbCl}_6^-$$

$$\text{(b) } \text{PTM}^+ + \text{H}_2\text{O} \rightarrow \underset{\text{I}}{(\text{C}_6\text{Cl}_5)_2\text{C}{=}\text{C}_6\text{Cl}_4{=}\text{O}} + \text{HCl} + \text{H}^+$$

$$\text{(c) } \text{SbCl}_3 + \text{Cl}_2 \rightarrow \text{SbCl}_5$$

Scheme VI

$$^•\text{PTM—PTM}^• \xrightarrow{\text{SbCl}_5} {}^+\text{PTM—PTM}^+\ 2\text{SbCl}_6^- \xrightarrow{\text{H}_2\text{O}} \underset{\text{II}}{\text{O}{=}\text{C}_6\text{Cl}_4{=}\text{C}(\text{C}_6\text{Cl}_5)\text{—C}_6\text{Cl}_4\text{—C}_6\text{Cl}_4\text{—C}(\text{C}_6\text{Cl}_5)\text{—C}_6\text{Cl}_4{=}\text{O}}$$

The synthesis of perchloro-$\alpha,\alpha,\alpha',\alpha'$-tetraphenylbi-*p*-tolyl-α,α'-diylium hexachloroantimonate ($^+$PTM-PTM$^+$ 2SbCl_6^-) has been carried out from diradical $^•$PTM-PTM$^•$ with SbCl_5 in SO_2Cl_2, the yield being 90.5% of theory. The UV–vis spectrum of this dication is almost coincident with that of PTM$^+$ (max, 670 nm vs 690,[8] supplementary material, Figure 5), evidencing the absence of any significant π–π electron interaction between its two molecular moieties.

While PTM$^+$ SbCl_6^- is relatively reluctant to hydrolysis, $^+$PTM-PTM$^+$ 2SbCl_6^- undergoes it easily (wet CH_2Cl_2), and even (slowly) in the air, giving an excellent yield of perchloro-α,α'-diphenyl-α,α'-bis(4-oxacyclohexadienylydene)bi-*p*-tolyl (II; perchlorodifuchsone), which has been characterized by elemental analysis, and infrared and UV–vis spectra. Again, the UV–vis spectrum of II is identical with that of I[8] (supplementary material, Figure 6). The high reactivity of $^+$PTM-PTM$^+$ is attributed to the electrostatic effect of its two positive charges (Scheme VI).

The Radical Ions. The radical ions $^•$PTM-Sp-PTM* (* = +, :$^-$) have been obtained as in Scheme VII by (1) mixing amounts of diradical and the diion salt; (2) partial oxidation of the diradical with SbCl_5; (3) partial oxidation of the dianion with I_2.

Scheme VII

$$\text{(1) } ^•\text{PTM-Sp-PTM}^• + {}^*\text{PTM-Sp-PTM}^* \rightarrow 2\,^•\text{PTM-Sp-PTM}^*$$

$$\text{(2) } ^•\text{PTM-Sp-PTM}^• \xrightarrow{\text{SbCl}_5} {}^•\text{PTM-Sp-PTM}^+$$

$$\text{(3) } ^-\text{:PTM-Sp-PTM:}^- \xrightarrow{\text{I}_2} {}^•\text{PTM-Sp-PTM:}^-$$

The reactivity differences between the radical ions and the need of additional relevant data required the individual strategies and treatments in their formation processes which are described next.

Perchloro-$\alpha,\alpha,\alpha',\alpha'$-tetraphenylbi-*p*-tolyl-α-yl-α'-ylium Radical Cation ($^•$PTM-PTM$^+$).[13] An equimolecular mixture of $^•$PTM-PTM$^•$ and $^+$PTM-PTM$^+$ 2SbCl_6^- in CH_2Cl_2 (Scheme VII, method 1; Sp = none), has been made to react for an extended period to ensure completion (66 h). The product consisted of a mixture of diradical, dicarbenium ion and $^•$PTM-PTM$^+$, since by subsequent

---

(13) Ballester, M.; Riera, J.; Castañer, J.; Pascual, I. *J. Am. Chem. Soc.* 1984, *106*, 3365 (preliminary communication).

Table I. ESR Data of Monoradicals, Diradicals, and Radical Ions

radical species	linewidth, G (solvent)	^{13}C hcc,^{a} G		
		α	bridgehead	ortho
PTM$\cdot$	1.43 (CCl_4)^b	29.5	12.7	10.7
III	1.25 (C_2Cl_4)	30.2	13.2	10.6
$\cdot$PTM-PTM$\cdot$	1.28 (CCl_4)^b 1.6 (CH_2Cl_2) 1.6 (THF)	29.1	13.2	9.5
$\cdot$PTM-C≡C-PTM$\cdot$	1.2 (CCl_4)^c 1.75 (THF)	28.3 -	12.2 -	10.2 -
$\cdot$PTM-CH_2CH_2-PTM$\cdot$	3.5 (THF)	-	-	-
$\cdot$PTM-PTM$^+$	0.8 (CH_2Cl_2)	14.8	6.4^d	5.3^d
$\cdot$PTM-C≡C-PTM$^+$	0.85 (CH_2Cl_2)	14.8	6.0^e	
$\cdot$PTM-CH_2CH_2-PTM$^+$	1.5 (CH_2Cl_2)	15.3	6.0^e	
$\cdot$PTM-PTM:$^-$	1.1 (THF)	14.8	5.5^e	
$\cdot$PTM-C≡C-PTM:$^-$	1.08 (THF)	14.0	5.2^e	
$\cdot$PTM-CH_2CH_2-PTM:$^-$	1.8 (THF)	15.0	6.0^e	

^{a} hcc = hyperfine coupling constants. ^{b} Reference 1. ^{c} Reference 11. ^{d} Data obtained from computer simulation. ^{e} Because of the hyperfine coupling constant halving.

hydrolysis, diradical, perchlorodifuchsone II and perchloro-α-(4-oxacyclohexadienylidene)-$\alpha,\alpha'\alpha'$-triphenylbi-*p*-tolyl-α'-yl radical (III; Scheme VIIIb) are obtained, the yields being 28 (recovery), 23, and 41% of theory, respectively. The radical fuchsone III was characterized by elemental analysis and IR, UV–vis, and ESR spectra (Table I). Magnetic susceptibility measurements indicate it is 98% pure. Its UV–vis absorption spectrum is closely similar to the superposition of fuchsone I and the radical PTM$\cdot$ spectra, or the superposition spectrum of the diradical $\cdot$PTM-PTM$\cdot$ and perchlorodifuchsone II (supplementary material, Figure 6). This again shows that the two molecular moieties of the perchlorobiphenyl derivatives behave as if they were electronically independent.

Therefore, a SET equilibrium is established (Scheme VIIIa). The equilibrium constant, calculated from that

Scheme VIII

$$\text{(a) }\cdot\text{PTM-PTM}\cdot + {}^+\text{PTM-PTM}^+ \rightleftharpoons 2\cdot\text{PTM-PTM}^+$$

$$\text{(b) }\cdot\text{PTM-PTM}^+ \xrightarrow{H_2O} O{=}C_6Cl_4{=}C(C_6Cl_5)\text{-}C_6Cl_4\text{-}C_6Cl_4\text{-}\dot{C}(C_6Cl_5)_2$$

III

$$\text{(c) }{}^+\text{PTM-PTM}^+ \xrightarrow{H_2O} \text{II}$$

equimolecular mixture of diradical and dication, is $K_{ET} \approx 2$. This system and the K_{ET} value have been reproduced by starting from an equimolecular mixture of diradical and $SbCl_5$ and adding a great excess of Cl_2 to revert the $SbCl_3$ formed back to $SbCl_5$ (see next).

Partial cationizations of diradical $\cdot$PTM-PTM$\cdot$ have carried out with $SbCl_5$ (Scheme VII, method 2; Sp = none), at room temperature, starting from variable molar ratios, and adding Cl_2 to maximize conversion of the diradical. Equilibria are reached ($\approx$6 h) (Scheme IX). As expected,

Scheme IX

$$\cdot\text{PTM-PTM}\cdot + 2SbCl_5 \rightleftharpoons \cdot\text{PTM-PTM}^+ + SbCl_6^- + SbCl_3$$

$$\cdot\text{PTM-PTM}^+ + 2SbCl_5 \rightleftharpoons {}^+\text{PTM-PTM}^+ + SbCl_6^- + SbCl_3$$

the degree of cationization increases as the relative proportion of $SbCl_5$ is raised, and thus it can be made nearly complete. The [$\cdot$PTM-PTM$^+$]/[$^+$PTM-PTM$^+$] ratio varies from 0.3 to 2.0, the larger the excess of $SbCl_5$ the lower the ratio.

ESR measurements were taken from a CH_2Cl_2 solution containing initially diradical $\cdot$PTM-PTM$\cdot$ and a substantial excess of $SbCl_5$ (Scheme VII, method 2; Sp = none). Shortly after the beginning, the diradical signal starts fading, being gradually replaced by a different, intense ESR signal which disappears in few hours (total conversion into the dication). The new ESR spectrum (Table I) corresponds to the radical cation, and it consists of two weak satellite line pairs due to coupling with aromatic (three bridgehead, six ortho) and the α ^{13}C in natural abundance (1.1%) (Figure 2).[3,14] Because of the proportion ($\approx$28%) of $\cdot$PTM-PTM$\cdot$ in equilibrium starting from an equimolecular mixture of this diradical and dicarbocation $^+$PTM-PTM$^+$ (Scheme VII, method 1; Sp = none), the ESR spectrum of radical cation $\cdot$PTM-PTM$^+$ cannot be entirely determined from the resulting mixture. Nevertheless, its most remarkable feature are the values of the ^{13}C hyperfine spin couplings (computer simulation) which are 6.4 (bridgehead), 5.3 (ortho)), and 14.8 G (α) (Table I), exactly half for those of monoradical PTM$\cdot$ (12.7, 10.7, and 29.5 G, respectively).[1,3] These constants show that the relevant spin densities in each radical cation moiety are half the "normal" values, i.e., those of PTM$\cdot$. Since the ESR linewidth in this highly chlorinated triphenylmethyl radicals arises mainly from unresolved hyperfine couplings with aromatic chlorine nuclei,[15] its value in the radical cation is also halved ($\cdot$PTM-PTM$\cdot$, 1.6 G; $\cdot$PTM-PTM$^+$, 0.8 G (Table I)).

Perchloro-$\alpha,\alpha,\alpha',\alpha'$-tetraphenylbi-*p*-tolyl-α,α'-diyl Radical Anion ($\cdot$PTM-PTM:$^-$).[16] The reaction between an equimolecular mixture of $\cdot$PTM-PTM$\cdot$ and 2(*n*-Bu)$_4$N^{+-}:PTM-PTM:$^-$ (Scheme VII, method 1; Sp = none) has been carried out in THF, at room temperature. For analytical purposes, the conversion of the prospective $\cdot$PTM-PTM:$^-$ formed, as well as the remaining dianion $^-$:PTM-PTM:$^-$ into the corresponding αH-compounds (*H*PTM-PTM*H* and $\cdot$PTM-PTM*H*) was effected with aqueous HCl (Scheme Xb). However, it has not been possible to separate $\cdot$PTM-PTM*H* from $\cdot$PTM-PTM$\cdot$ and *H*PTM-PTM*H*, even using HPLC, and therefore the re-

Scheme X

$$\text{(a) }\cdot\text{PTM-Sp-PTM}\cdot + {}^-\text{:PTM-Sp-PTM:}^- \rightleftharpoons 2\cdot\text{PTM-Sp-PTM:}^-$$

(Sp = none, C≡C, CH_2CH_2)

$$\text{(b) }{}^-\text{:PTM-PTM:}^- \xrightarrow{H^+} H\text{PTM-PTM}H$$

$$\cdot\text{PTM-PTM:}^- \xrightarrow{H^+} (C_6Cl_5)_2\dot{C}\text{-}C_6Cl_4\text{-}C_6Cl_4\text{-}CH(C_6Cl_5)_2$$

$\cdot$PTM-PTM*H*

$$\text{(c) }\cdot\text{PTM-PTM}H \xrightarrow{SbCl_5} (C_6Cl_5)_2\overset{+}{C}\text{-}C_6Cl_4\text{-}C_6Cl_4\text{-}CH(C_6Cl_5)_2 \xrightarrow{H_2O}$$

IV

$$O{=}C_6Cl_4{=}C(C_6Cl_5)\text{-}C_6Cl_4\text{-}C_6Cl_4\text{-}CH(C_6Cl_5)_2$$

V

---

[14] Falle, H. R.; Luckhurst, G. R.; Horsfield, A.; Ballester, M. *J. Chem. Phys.* **1969**, *50*, 258.

[15] Reference 3, pp 431, 436.

[16] Ballester, M.; Pascual, I. *Tetrahedron Lett.* **1985**, *26*, 5589 (preliminary communication).

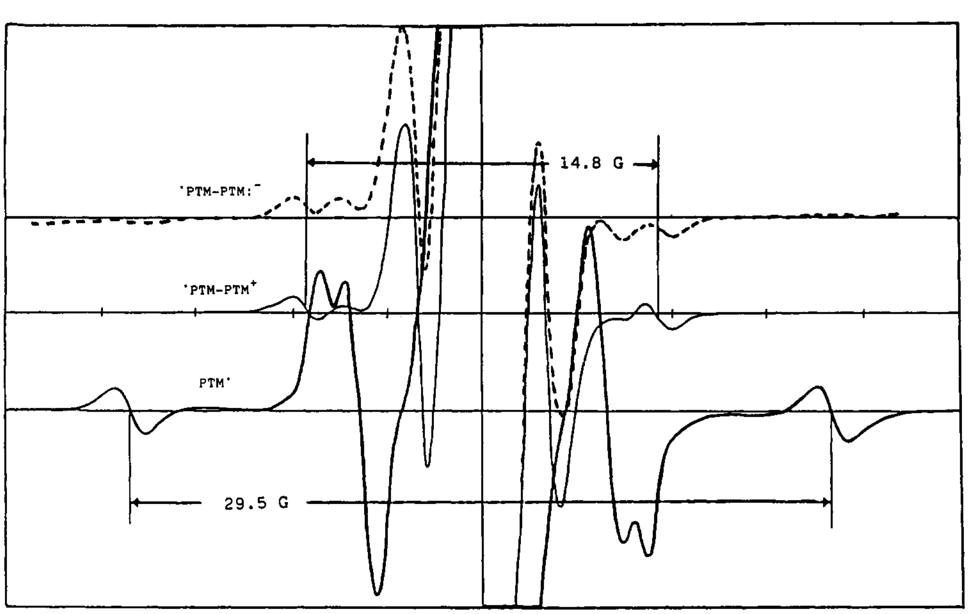


Figure 2. ESR spectra of radical ions ·PTM-PTM$^+$ (—) and ·PTM-PTM:$^-$ (- - -), showing the halving of α and aromatic ^{13}C hyperfine couplings, with respect to those of radical PTM· (—).

sulting reaction mixture was submitted to oxidation with $SbCl_5$ in SO_2Cl_2 at room temperature to convert these two radicals to difuchsone II and αH-fuchsone V (Scheme Xc) which presumably could be separated. Unfortunately, this oxidation *is not complete*, even using a huge excess of $SbCl_5$. This unexpected result might be due to the enhanced electrophilicity of dication $^+$PTM-PTM$^+$, as compared to that of PTM$^+$. Nevertheless, the major product is ·PTM-PTM$^+$, as inferred from TLC of the oxidation mixture.

The ESR spectrum of the initial mixture of diradical ·PTM-PTM· and dianion $^-$:PTM-PTM:$^-$ in THF, at room temperature (Figure 2) is consistent with the results above. It is the overlap of two spectra, the predominant one being provided with ^{13}C hyperfine coupling constants (aromatic, 5.4 G; α, 14.8 G) and linewidth (1.1 G) (Table I) which are half the normal values, as in the radical cation ·PTM-PTM$^+$. This shows the presence of radical anion ·PTM-PTM:$^-$. The second spectrum corresponds to "normal" ^{13}C couplings and, therefore, is attributed to diradical ·PTM-PTM·. The radical anion/diradical molar ratio has been calculated from the relative ^{13}C line intensities (taking into account the narrowing of the ^{13}C lines); its value is approximately 8, and it remains constant for hours. It corresponds to a SET equilibrium constant $K_{ET} \approx 64$ (Scheme Xa; Sp = none).

The UV–vis spectrum of an equimolecular mixture of diradical ·PTM-PTM· and dianion $^-$:PTM-PTM:$^-$ in THF, at room temperature, is coincident with that corresponding to an equimolecular addition of ·PTM-PTM· and $^-$:PTM-PTM:$^-$ (Figure 3a; Table II). This again indicates that the two structural moieties of radical anion ·PTM-PTM:$^-$ are electronically independent.

By gradually adding I_2 to $2(n\text{-}Bu)_4N^+$ $^-$:PTM-PTM:$^-$ (Scheme VII, method 3; Sp = none), in THF, the ESR spectra corresponding to mixtures of the diradical ·PTM-PTM· and radical anion ·PTM-PTM:$^-$ are observed. The signal of the latter decreases with the amount of I_2 added, a substantial excess of the latter causing its disappearance.

Osmometric measurements have been performed on an equimolecular mixture of diradical ·PTM-PTM· and dianion $^-$:PTM-PTM:$^-$ salt in THF ($\approx 7.5 \times 10^{-3}$ mol L^{-1}), the mean molecular weight found being 1270 (·PTM-PTM·, 1449). From the osmometric data on the salt, given before, and the ESR ^{13}C radical anion/diradical signal ratio, it has been estimated that the radical anion is 65% as ion pair with its counterion, the rest 35% being free radical anion. Therefore, the ion pair dissociation constant is K_D = 0.19 mol L^{-1}. This result contrasts with that obtained from carbanions XPTM:$^-$ which, under about the same conditions, exist entirely as ion pairs.[4]

Table II. UV–Vis Absorptivity Values

nm	ϵ_1 (diradical)	ϵ_2 (dianion)	$\epsilon_1 + \epsilon_2$	ϵ_{obs}
	·PTM-PTM·/$^-$:PTM-PTM:$^-$ (Figure 3a)			
383	76500	5500	82000	81500 (max)
417	4000	8000	12000	13000 (min)
520	2500	59500	62000	59500 (max)
	·PTM-CH_2CH_2-PTM·/$^-$:PTM-CH_2CH_2-PTM:$^-$ (Figure 3b)			
383	70000	7000	77000	76500 (max)
415	3000	9500	12500	13000 (min)
517	2500	56500	59000	59000 (max)

Perchloroethynylenebis(4-triphenylmethyl) Radical Cation (·PTM-C≡C-PTM$^+$). This radical cation is formed when $SbCl_5$ is added, to diradical ·PTM-C≡C-PTM· in CH_2Cl_2, at room temperature (Scheme VII, method 2; Sp = C≡C). In fact, the ESR main-line observed shows a linewidth of 0.85 G (Table I); i.e., half the value for its parent diradical (1.75 G) (see over). Also, the ^{13}C coupling constant values are halved with respect to those of the PTM monoradicals, being similar to those of ·PTM-PTM$^+$ (α, 14.4; aromatic, ≈6 G) (Figure 4a; Table I). By adding an adequate excess of $SbCl_5$, ·PTM-C≡C-PTM$^+$ becomes the main radical component.

Perchloroethynylenebis(4-triphenylmethyl) Radical Anion (·PTM-C≡C-PTM:$^-$). The tetra-n-butylammonium salt of this Radical Anion has been obtained by both methods 1 and 3 (Scheme VII; Sp = C≡C). A mixture of diradical ·PTM-C≡C-PTM· and a massive excess of dianion $^-$:PTM-C≡C-PTM:$^-$ (method 1) gives radical anion ·PTM-C≡C-PTM:$^-$ as the sole radical specie, its ESR main-line width being 1.08 G and the ^{13}C coupling constants being 14.0 (α) and 5.2 G (aromatic) (Table I; Figure 4a). A mixture of diradical and dianion in a 0.5 molar ratio, in THF, gives the radical anion, main-line width, 1.2 G. Since the width of the diradical is 2.0 G, it is concluded that the proportion of radical anion formed is 90%, approximately. Radical anion ·PTM-C≡C-PTM:$^-$

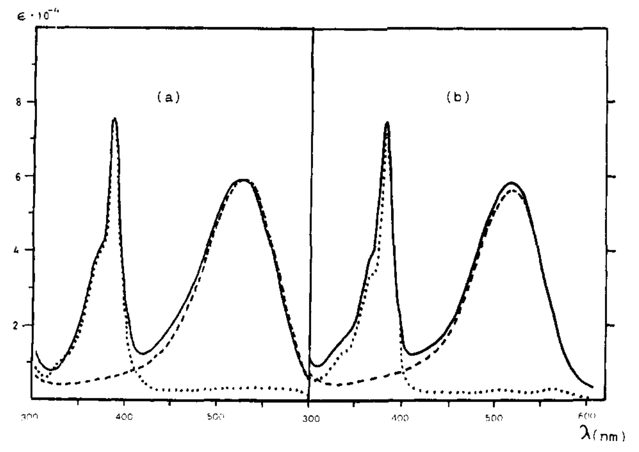


Figure 3. UV–vis spectra of radical anions: (a) •PTM-PTM• (···), $^-$:PTM-PTM:$^-$ (– – –), •PTM-PTM:$^-$ (—), (b) •PTM-CH$_2$CH$_2$-PTM• (···), $^-$:PTM-CH$_2$CH$_2$-PTM:$^-$ (– – –), •PTM-CH$_2$CH$_2$-PTM:$^-$ (—).

is also obtained in about a 90% yield (linewidth, 1.2 G) by adding a minor proportion of I$_2$ to a solution of $^-$:PTM-C≡C-PTM:$^-$ in THF (method 3).

1,2-Ethylenebis(4-tetradecachlorotriphenylmethyl) Radical Cation (•PTM-CH$_2$CH$_2$-PTM$^+$). The ESR spectrum of a mixture of diradical •PTM-CH$_2$CH$_2$-PTM• and a slight excess of SbCl$_5$ in CH$_2$Cl$_2$ (Scheme VII, method 2; Sp = CH$_2$CH$_2$) shows ^{13}C couplings of 15.3 (α) and ≈6.0 G (aromatic) of radical cation •PTM-CH$_2$CH$_2$-PTM$^+$. The observed main-line width is 1.5 G, and since that of the diradical is twice this value (2.9 G), it is concluded that the diradical is nearly absent (Table I). As the reaction time elapses the ESR signal fades away (conversion to dication $^+$PTM-CH$_2$CH$_2$-PTM$^+$).

1,2-Ethylenebis(4-tetradecachlorotriphenylmethyl) Radical Anion (•PTM-CH$_2$CH$_2$-PTM:$^-$). This radical anion results from a mixture of diradical •PTM-CH$_2$CH$_2$-PTM• and dianion $^-$:PTM-CH$_2$CH$_2$-PTM:$^-$ in THF (Scheme VII, method 1; Sp = CH$_2$CH$_2$), at room temperature. When the dianion is present in a very large excess, the resulting ESR spectrum is that of •PTM-CH$_2$CH$_2$-PTM:$^-$, the linewidth being 1.8 G (Table I). The same ESR spectrum is obtained by employing equimolecular mixtures of those components, showing that the equilibrium between the diradical/dianion and the radical anion is almost completely shifted toward the latter. The ^{13}C coupling constants are 15.0 (α) and ≈6 G (aromatic) (Figure 4b; Table I). The UV–vis spectrum of the radical-anion is coincident with the mean spectrum of the diradical and the dianion (Figure 3b; Table II), as in •PTM-PTM:$^-$. •PTM-CH$_2$CH$_2$-PTM:$^-$ has also been obtained by method 3 (Scheme VII; Sp = CH$_2$CH$_2$), from the dianion and I$_2$, in THF.

Mechanistic and Structural Aspects of the Spin–Charge Exchange. A priori, three structural possibilities for radical ions •PTM-Sp-PTM* are possible: (A) A single molecular structure with weakly interacting radical and ionic moieties (Scheme XIA). (B) A single molecular structure where both the charge and the electron spin are fully delocalized affording two equivalent molecular moieties (symmetrical charge and spin delocalization) (Scheme XIB). (C) Two equivalent structures of type A in equilibrium (Scheme XIC).

Scheme XI

(A) •PTM-Sp-PTM* $\not\rightleftharpoons$ *PTM-Sp-PTM•

(B)•PTM-Sp-PTM* ↔ *PTM-Sp-PTM•

(C) •PTM-Sp-PTM* $\rightleftharpoons$ *PTM-Sp-PTM•

(* = + or :$^-$)

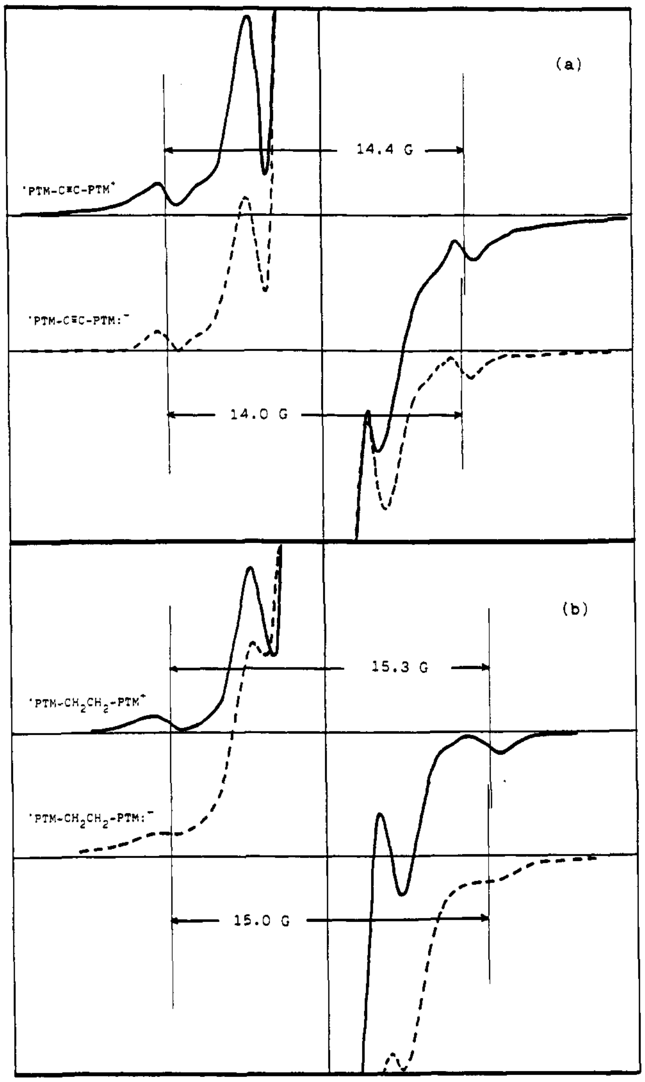
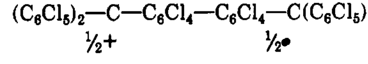


Figure 4. ESR spectra of radical anions and corresponding radical cations showing their halved α and aromatic ^{13}C hyperfine coupling constants.

The ESR linewidth in these highly chlorinated triphenylmethyl radicals arises mainly from unresolved ^{35}Cl and ^{37}Cl lines.[15] The ^{13}C hyperfine couplings are proportional to the spin densities on the relevant carbons.[17] Therefore, the halving of the ESR linewidth and ^{13}C hyperfine coupling constant values observed in all the radical ions being dealt with here, with respect to those of PTM• and other PTM radicals and diradicals (•PTM-PTM•, 1.6 G; •PTM-PTM$^+$, 0.8; Table I), indicates that the spin densities on the chlorines and the carbons, i.e., on their molecular moieties, are halved (Table I):



$$(C_6Cl_5)_2\overset{1/2\bullet}{\underset{1/2+}{C}}-C_6Cl_4-C_6Cl_4-\overset{1/2+}{\underset{1/2\bullet}{C}}(C_6Cl_5)_2$$

This rules out structure A.

---

[17] Ayscough, P. B. *Electron Spin Resonance in Chemistry*; Methuen: London, 1967; p 60. Carrington, A.; McLachlan, A. D. *Introduction to Magnetic Resonance*, Chapman and Hall: London, 1979; p 80.

On account of the symmetrical molecular odd-electron and electric charge distribution, the UV–vis spectrum of system B should differ much from that of the PTM radicals,[1,4] anions,[4,18] and cations,[8,9] which in turn are dramatically unlike each other, but, as already mentioned, it actually is the mean spectrum of the radical and the ionic moieties. This rules out structure A. In addition, it is stressed that the UV–vis spectrum of perchlorobiphenyl derivatives shows with no exception a total steric inhibition of (biphenyl) resonance between molecular moieties,[1,3] as found in perchlorobiphenyls,[19] difuchsone II (supplementary material, Figure 6), radical fuchsone III (supplementary material, Figure 6), diradical ${}^{\bullet}$PTM-PTM${}^{\bullet}$ (Figure 1a), dication ${}^{+}$PTM-PTM^{+} (supplementary material, Figure 5), and ${}^{-}$:PTM-PTM:${}^{-}$ (Figure 1b). These considerations are compelling evidence against B in radical ions ${}^{\bullet}$PTM-PTM:${}^{-}$ and ${}^{\bullet}$PTM-CH_2CH_2-PTM:${}^{-}$, the UV–vis spectral curves of which are, as pointed out here earlier, coincident (wavelengths and absorptivities) with the mean spectral curve between those of diradical ${}^{\bullet}$PTM-PTM${}^{\bullet}$ and dianion ${}^{-}$:PTM-PTM:${}^{-}$ (Figure 3a), and diradical ${}^{\bullet}$PTM-CH_2CH_2-PTM${}^{\bullet}$ and dianion ${}^{-}$:PTM-CH_2CH_2-PTM:${}^{-}$ (Figure 3b), respectively. As pointed out earlier in the discussion of diradical ${}^{\bullet}$PTM-PTM${}^{\bullet}$, the reason for such an additivity resides in the repulsions among the four chlorines ortho with respect to the (central) biphenyl bond, which cause the two phenyl rings of the biphenyl system to be each other perpendicular.

System C accounts for the both the UV–vis and the ESR ^{13}C hyperfine coupling constants and linewidths, providing the rate of equilibration is very fast (rate > 10^8 s^{-1}). Then the "slow" ESR technique "sees" therefore the time-averaged spin distribution, half the "normal" (PTM${}^{\bullet}$) values, while the actual radical ion species is revealed by the "fast" UV–vis technique.

The spin–charge exchanges described here may be included in the so-called "intramolecular long-distance electron transfers".[20] The distance between spin centers in rigid diradicals ${}^{\bullet}$PTM-PTM${}^{\bullet}$ and ${}^{\bullet}$PTM-C≡C-PTM${}^{\bullet}$, calculated from D, the triplet ESR zero-field-splitting parameter, are 8.2 and 11.3 Å,[22] respectively (those between their two α-carbons, the "structural centers", are 10 and 14 Å). On account of the perpendicularity of the two benzene rings in the octachlorobiphenyl system of radical ions ${}^{\bullet}$PTM-PTM^{+} and ${}^{\bullet}$PTM-PTM:${}^{-}$, the overlap involving the higher energy bonding π-orbitals is practically nonexistent, as shown by the various examples of UV–vis spectrum commented here (complete steric inhibition of resonance). Therefore, it is doubtful that any through-π-bond mechanism might be involved in those spin–charge exchanges, since it can hardly provide a low-energy path for them. In contrast, it is well-known that σ-bonds are essentially not subject to such an inhibition. In fact, Dewar[23] and Hoffmann[24] have shown theoretically that, as far as electronic conjugation is concerned, there is no basic difference between saturated molecules and ones containing π-bonds. On account of the flexibility of its CH_2CH_2 spacer, radical ion ${}^{\bullet}$PTM-CH_2CH_2-PTM* (* = –, +) is not a rigid radical ion, and consequently there exists a definite possibility of a spin–charge exchange where the separation between the spin and the charge centers be much smaller than 8.2 Å. Nevertheless, this does not rule out the σ-path mechanism. As far as rigid radical ion ${}^{\bullet}$PTM-C≡C-PTM*, π-electron conjugation with the triple bond occurs, as indicated by its UV–vis spectrum (see before). However, the relevant extended π-MOs for each molecular moiety are most probably orthogonal,[11a] as in ${}^{\bullet}$PTM-PTM:${}^{-}$ and ${}^{\bullet}$PTM-PTM^{+}. Therefore, at least some spin–charge exchanges here described take place along σ-paths. This conclusion has also been reached from the study of some intramolecular SETs involving feudal[3,7] radical anions provided with rigid "spacers", where the electric charge is not exchanged but transferred along with the odd-electron occupying an antibonding MO.[21]

The spin–charge exchange in the allodial[3,7] radical ions here described, where the odd-electron occupies a bonding orbital, cannot take place by an intermolecular SET mechanism between the diradical and the diion since such a process should be slow, so much that in closely related cases it takes minutes to reach equilibration.[4] In fact, under the conditions here described, the ESR main linewidth and the ^{13}C hyperfine coupling constants of equimolecular mixtures of radical PTM${}^{\bullet}$ and PTM:${}^{-}$, and PTM${}^{\bullet}$ and PTM^{+}, and, in general, mixtures of PTM radicals and PTM anions[4] do not differ from those of pure PTM radicals. Moreover, as mentioned earlier, it has recently been found that the intermolecular SETs between PTM radicals and PTM anions are relatively slow processes.[4]

A significant subject is the involvement of the counterions $SbCl_6^-$ and $(n\text{-Bu})_4N^+$ in the radical ion exchange process. Taking into account that the dissociation constant of the radical anion ${}^{\bullet}$PTM-PTM:${}^{-}$ is 0.19 mol L^{-1} under the much higher dilution (60 times) of the ESR measurements conditions ($\approx 1.25 \times 10^{-4}$ mol L^{-1}) ion pairs should be almost completely dissociated (≈92%) to free ions, and consequently, the observed ESR spectrum should be that of the free radical anion, exclusively. Therefore, the counterion does not appear to play any significant role in the spin–charge exchange. A correlation between the electron and the counterion would reduce greatly the normal rate of electron transfer,[25] and therefore, there would be a flattening of the ^{13}C hyperfine lines not observed. In the limiting case, where the counterion would stay put at a radical ion moiety, the resulting asymmetry in spin distribution of the moieties would cause two independent, superimposed ESR hyperfine spectra, not observed either.

In this connection it is emphasized that there is a chemical proof for the presence of ion pairs of salt PTM^{+} $AlCl_4^-$ in solution, although there is no evidence that it might occur with PTM^{+} $SbCl_6^-$.[26-28] Therefore, the preceding conclusions could reasonably be extended to the radical cation ${}^{\bullet}$PTM-PTM${}^{\bullet}$ dealt with here.

It is pointed out that the equilibrium between diradical/dianion and the radical anion (Scheme Xa) gives predominantly (80–90%) the latter, while that involving radical cation ${}^{\bullet}$PTM-PTM^{+} is a balanced one (Scheme VIIIA). It is reasonable to assume that the solvent (CH_2Cl_2 and THF) plays a major role in those equilibria differences.

Finally, it is stressed that the clear-cut, dramatic effect of the intramolecular electron-transfer equilibrium described here allows its straightforward, unambiguous in-

---

(18) Ballester, M.; de la Fuente, G. *Tetrahedron Lett.* **1970**, 4509.

(19) Ballester, M.; Castañer, J.; Riera, J. *An. Quim.* **1977**, *73*, 546. Reference 3, p 414.

(20) For a general review, see ref 21 and references therein.

(21) Closs, G. L.; Miller, J. R. *Science* **1988**, *240*, 440.

(22) Wasserman, E.; Ballester, M.; et al., unpublished.

(23) Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 669.

(24) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1.

(25) Reference 6, p 388.

(26) Ballester, M.; Olivella, S. *Polychloroaromatic Compounds*; Suschitzky, H., Ed.; Plenum Press: London, 1974; pp 104, 130.

(27) Ballester, M.; Castañer, J.; Riera, J.; Pujadas, J.; Armet, O.; Onrubia, C.; Rio, J. A. *J. Org. Chem.* **1984**, *49*, 770.

(28) Ballester, M.; Riera, J.; Castañer, J.; Carreras, C.; Ubierna, J. J.; Badía, C. *J. Org. Chem.* **1989**, *54*, 4611.

terpretation. In fact, the majority of studies on feudal radical ions described[29-31] suffer not only from severe problems due to their chemical aggressiveness and thermal instability but from hyperfine spectrum complexity as well. In contrast, perchlorination not only enhances tremendously the thermal and chemical stability of organic substrates but, on account of the low nuclear magnetic moment of chlorine (^{35}Cl, 0.822 and ^{37}Cl, 0.684 μ_N vs ^{1}H, 2.793), it limits drastically the number of ESR hyperfine lines, and consequently allows simple and direct interpretation of the physical phenomena lying behind, as in the study of the paramagnetic species dealt with here.

Experimental Section

General Methods and Equipment. The IR, UV–vis, and ESR spectra have been recorded with Perkin-Elmer Model 682, Beckman Acta M-VI and Perkin-Elmer Model Lambda array 3840, and Varian Model E109 spectrometers, respectively. The osmometric measurements have been performed with a V.P. Knauer osmometer Model 73111. The ESR ^{13}C coupling constants have been calculated by computer simulation, using programs devised by the authors specifically, including Gauss–Lorentz hybrid line shapes. A HPLC chromatograph Perkin-Elmer 3B, provided with an UV–vis detector LC-75 and a column LC-100, was used.

The formation of the radical ions have been carried out in the dark. To prevent hydrolysis in the processes involving carbenium ions, the air was replaced by argon.

Since the IR spectra differ markedly from their nonchlorinated counterparts, those of the species dealt with here are included.

Reversion of PTM$^+$ SbCl$_6^-$ to PTM$^\bullet$ with SbCl$_3$. (a) To a solution of PTM$^+$ SbCl$_6^-$, prepared as described[9] (0.024 g), in CH$_2$Cl$_2$ (3 mL) was added a great excess of SbCl$_3$, and the resulting solution was left undisturbed (4 h). The reaction mass was treated with water, the CH$_2$Cl$_2$ layer was washed with aqueous HCl and with water, dried, and evaporated to dryness. The residue, dissolved in CHCl$_3$, was passed through silica gel and next submitted to HPLC, giving fuchsone I (35%) and radical PTM$^\bullet$ (65%). (b) A homogeneous solid mixture of PTM$^+$ SbCl$_6^-$ and SbCl$_3$ was let stand (2 h) in argon. The resulting solid was dissolved in wet CH$_2$Cl$_2$, and the solution was treated as in a, yielding fuchsone I (8%) and radical PTM$^\bullet$ (92%).

Perchloro-*α,α,α′,α′*-tetraphenylbi-*p*-tolyl-*α,α′*-diylium Hexachloroantimonate ($^+$PTM-PTM$^+$ 2SbCl$_6^-$). Diradical $^\bullet$PTM-PTM$^\bullet$[1] (0.109 g, 7.5 × 10^{-5} mol) was dissolved, at room temperature, in SO$_2$Cl$_2$ (20 mL), and next a great excess of SbCl$_5$ (0.48 g; 1.6 × 10^{-3} mol) was added, letting it stand for 3 days. To the resulting mass was added anhydrous CCl$_4$ (15 mL) gradually (5 days), small deep-green crystals of the title dication salt being formed, which were separated, washed with anhydrous CCl$_4$, and dried (70 °C; under vacuum) (0.144 g; 90.5% yield). This salt undergoes rapid hydrolysis in the air, and consequently good analyses and IR spectra cannot be obtained. Its UV–vis spectrum has been taken in concentrated H$_2$SO$_4$ (295 (sh), 393 (vw), 435 (vw), 670 nm)), and it is practically coincident with that of PTM$^+$ SbCl$_6^-$ (supplementary material, Figure 5).[8] Identification has been completed by hydrolysis.

Hydrolysis of $^+$PTM-PTM$^+$ 2SbCl$_6^-$. This salt (0.098 g) was shaken at room temperature with wet CH$_2$Cl$_2$; an immediate color change from green to orange was observed. The resulting solution was washed with aqueous concentrated HCl and with water and dried over anhydrous Na$_2$SO$_4$. The residue, resulting from evaporation of the solvent, was dissolved in CCl$_4$ and filtered through activated silica gel. The resulting adsorbate was eluted with chloroform, giving perchloro-*α,α′*-diphenyl-*α,α′*-bis(4-oxacyclohexadienylidene)bi-*p*-tolyl (difuchsone II; 0.060 g): yield 92%; very small orange crystals; mp 339–41 °C; UV–vis (CHCl$_3$) (supplementary material, Figure 6) 285 (sh) nm, 418 (ϵ 18 500, 43 000); IR (KBr) 1660, 1558, 1508, 1460, 1340, 1330, 1300, 1250, 1220, 1128, 1110, 1020, 860, 835, 775, 765, 750, 740, 730, 680, 540, 510 cm^{-1}. Anal. Calcd for C$_{38}$Cl$_{26}$O$_2$: C, 32.4; H, 0.0. Found: C, 32.7; H, 0.2.

Synthesis of Dicarbanion Salts $^-$:PTM-Sp-PTM:$^-$. The dicarbanions may be synthesized from two different precursors: Method a from the di-*αH*-compounds *H*PTM-Sp-PTM*H* (≈6.3 × 10^{-4} mol) and Method b from the diradicals $^\bullet$PTM-Sp-PTM$^\bullet$ (≈1.5 × 10^{-4} mol). These reaction have been performed in THF (20–100 mL) and at room temperature by adding a substantial excess of (*n*-Bu)$_4$N$^+$ HO$^-$ (3.0 × 10^{-3}–1.3 × 10^{-2} mol), and shaking (2 h) the mass in an ultrasonic bath. The resulting solution is poure into and washed (by centrifugation) with an 1:1 hexane/water (40–200 mL) mixture. The dark oily bottom layer is dissolved in a small amount of THF, some hexane or hexane/ethyl ether is added (to assist complete elimination of the THF), and the mixture is evaporated to dryness (high vacuum, 70 °C). In the synthesis of 2(*n*-Bu)$_4$N$^+$ $^-$:PTM-C≡C-PTM:$^-$, instead of centrifuging, the organic layer is washed with water, evaporated, digested with hexane, and evaporated to dryness (100 °C; high vacuum).

Tetra-*n*-butylammonium Perchloro-*α,α,α′,α′*-tetraphenyl-bi-*p*-tolyl-*α,α′*-diyl Dianion (2(*n*-Bu)$_4$N$^+$ $^-$:PTM-PTM:$^-$). Method a from *H*PTM-PTM*H*:[1] yield, 98.6%; dark-garnet solid; mp 112–114 °C; UV–vis (THF) (Figure 1b) 383 nm, 525 (ϵ 4000, 59 500); IR (KBr) 2960, 2940, 2880, 1650–1620, 1545, 1515, 1500, 1480–1460, 1420, 1360, 1330, 1300, 1220, 1210, 1020–1005, 870, 830, 800, 732, 720, 682, 645, 610, 580, 520, 500 cm^{-1}. Anal. Calcd for C$_{70}$H$_{72}$Cl$_{28}$N$_2$: C, 43.5; H, 3.7; Cl, 51.3; N,1.4. Found: C, 43.8; H, 3.7; Cl, 49.2; N, 1.2. **Method b from $^\bullet$PTM-PTM$^\bullet$:**[1] yield 87.4%.

Tetra-*n*-butylammonium Perchloroethynylenebis(4-triphenylmethide) (2(*n*-Bu)$_4$N$^+$ $^-$:PTM-C≡C-PTM:$^-$). Method b from $^\bullet$PTM-C≡C-PTM$^\bullet$:[11] yield, 94.5%; dark blue-green solid; mp 176–179 °C; UV–vis (THF) (Figure 1b) 305 (sh) nm, 345 (sh), 385, 515, 665 (ϵ 23 900, 15 200, 10 300, 40 400, 82 800); IR (KBr) 2130, 1545, 1540, 1530, 1515–1505, 1480, 1427, 1345, 1332, 1295, 1250, 1205, 1126, 1102, 1040, 955, 852, 810, 740, 730, 720, 692, 680, 643, 605, 580, 515, 475 cm^{-1}. Anal. Calcd for C$_{72}$Cl$_{28}$H$_{72}$N$_2$: C, 44.2; H, 3.7; N, 1.4. Found: C, 45.1; H, 4.1; N, 1.3.

Tetra-*n*-butylammonium 1,2-Ethylenebis(4-tetradecachlorotriphenylmethide) (2(*n*-Bu)$_4$N$^+$ $^-$:PTM-CH$_2$CH$_2$-PTM:$^-$). Method b from $^\bullet$PTM-CH$_2$CH$_2$-PTM$^\bullet$:[10] yield, 78%; dark-garnet solid; mp 124–127 °C; UV–vis (THF) (Figure 1b) 517 nm (ϵ 56 700); IR (KBr) 3705, 2960, 2930, 2870, 1540, 1515, 1500, 1470, 1465, 1375, 1357, 1330, 1207, 1135, 1027, 875, 800, 725, 715, 675, 660, 650, 640, 630, 605, 580, 530, 520 cm^{-1}. Anal. Calcd for C$_{72}$Cl$_{28}$H$_{76}$N$_2$: C, 44.1; H, 3.9; N, 1.4. Found: C, 43.5; H, 3.9; N, 1.4.

Preparation of the Radical Ions. General Procedures: (a) Radical Cations. The diradical (7–9 mg) is dissolved in purified CH$_2$Cl$_2$ (5 mL), in an ultrasonic bath. About 1 mL of the solution is transferred to the ESR cell, degassed, and, at room temperature, under argon, a solution of SbCl$_5$ in CH$_2$Cl$_2$ (0.2 mL; ≈6 × 10^{-2} mmol) is added, the ESR spectrum being taken immediately. **(b) Radical Anions.** First procedure: The dianion salt (≈4 mg) is dissolved in purified THF (2–3 mL), and ≈1 mL of the resulting solution is transferred to the ESR cell, degassed and, at room temperature, under argon, a solution of I$_2$ in THF (0.2 mL, ≈5 × 10^{-4} mmol) is added, the ESR spectrum being taken immediately. Second procedure: Equal volumes of a solution of the dianion (4.7–4.9 mg) in THF (10 mL), and of a solution of the corresponding diradical (3.6–3.8 mg) in the same solvent (10 mL) are mixed at room temperature. About 1 mL of the resulting solution is transferred to an ESR cell, degasified, and its ESR spectrum is taken under argon. 2 mL of the same solution are diluted with THF to 10 mL, and the UV–vis spectrum is taken immediately and after 8 h.

The Reaction of Perchloro-*α,α,α′,α′*-tetraphenylbi-*p*-tolyl-*α,α′*-diylium Hexachloroantimonate ($^+$PTM-PTM$^+$ 2SbCl$_6^-$) with Perchloro-*α,α,α′,α′*-tetraphenylbi-*p*-tolyl-*α,α′*-diyl Diradical ($^\bullet$PTM-PTM$^\bullet$). A mixture of $^+$PTM-PTM$^+$ 2SbCl$_6^-$ (0.144 g, 6.9 × 10^{-5} mol) and $^\bullet$PTM-PTM$^\bullet$[1] (0.10 g, 6.8 × 10^{-5} mol) in anhydrous methylene chloride (10 mL) was shaken (66 h) at room temperature under argon. Water (1 mL) was then added, and the resulting mixture was washed with aqueous HCl acid and dried. The solid residue (0.184 g), obtained by evapo-

---

[29] Weissman, S. I. *J. Am. Chem. Soc.* **1958**, *80*, 6462.

[30] Harriman, J. E.; Maki, A. H. *J. Chem. Phys.* **1963**, *39*, 778.

[31] Ohya, H. O.; Terahara, A.; Hirota, N.; Sakata, Y.; Misumi, S. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1782.

ration to dryness, was submitted to TLC in chloroform giving (decreasing R_fs) diradical •PTM-PTM• (0.056 g, 28% recovery), fuchsone radical III (0.08 g, 41% yield), and difuchsone II (0.044 g, 23%). III: orange-red solid; mp 316–319 °C dec; UV-vis ($CHCl_3$) (supplementary material, Figure 6) 285 nm, 365 (sh), 385, 420, 560 (ϵ 15 500, 29 400, 53 300, 23 000, 1240); IR (KBr) 1660, 1650, 1550, 1500, 1350, 1330, 1290, 1255, 1220, 1125, 1105, 1015, 875, 865, 835, 812, 765, 755, 730, 700, 675, 650, 620–600, 535, 530, 508 cm^{-1}. ESR data: Table I. Magnetic susceptibility $X_{dia} = -0.488 \times 10^{-6}$ emu;[32] $J = -4.7$ K, $\mu = 1.71$, spin/mol = 5.92×10^{23}. Anal. Calcd for $C_{38}Cl_{27}O$: C, 31.9; H, 0.0. Found: C, 32.2; H, 0.0.

Conversion of Fuchsone Radical III into Difuchsone II. A solution of $SbCl_3$ (0.24 g, 1.1×10^{-3} mol) in CH_2Cl_2 (25 mL) was saturated with Cl_2 at room temperature, and next fuchsone radical III (0.045 g, 3.1×10^{-5} mol) was added. After stirring (24 h), water (5 mL) was added, and the CH_2Cl_2 layer was washed with aqueous HCl and dried. The solid residue (0.046 g), obtained by evaporation to dryness, was submitted to column chromatography in CCl_4, giving difuchsone II (0.043 g, 97% yield), which was identified by comparative TLC and IR.

Acknowledgment. Thanks are due to Drs. E. Wasserman, J. S. Miller, and P. Krusic, E. I. DuPont de Nemours (Wilmington, DE) for providing us with complementary ESR data, to Mrs. A. Díez for the ESR measurements, and to Mr. J. Vidal for his experimental assistance. I.P. wishes to express her gratitude to the Spanish Ministry of Education and Science for a doctoral fellowship during the period 1985–1989.

Supplementary Material Available: UV-vis spectra of cations (Figure 5) and of fuchsone I and difuchsone II (2 pages). Ordering information is given on any current masthead page.

---

(32) Calculated independently from modified Pascal's data.[33]

(33) Foex, G.; Goreter, C.; Smith, L. J. *Constants Selectionées. Diamagnetisme et Paramagnetisme. Relaxation Paramagnêtique*; Masson et Cie.: Paris, 1957, pp 222–225. Ballester, M.; Castañer, J.; Riera, J.; Ibáñez, A.; Pujadas, J. *J. Org. Chem.* **1982**, *47*, 259.

Macrocyclic Trinucleating Ligands for the Cocomplexation of Two "Soft" (Cu^{2+}, Ni^{2+}, or Zn^{2+}) Metal Centers and One "Hard" (Ba^{2+} or Cs^{+}) Metal Center[1]

Frank C. J. M. van Veggel,[†] Martinus Bos,[‡] Sybolt Harkema,[§] Henry van de Bovenkamp,[†]
Willem Verboom,[†] Jan Reedijk,[⊥] and David N. Reinhoudt*,[†]

Laboratories of Organic Chemistry, Chemical Analysis, and Chemical Physics, University of Twente,
P.O. Box 217, 7500 AE Enschede, The Netherlands, and Department of Chemistry, Gorlaeus Laboratories,
Leiden University, 2300 RA Leiden, The Netherlands

Received June 27, 1990

Macrocyclic heterotrinucleating ligands that have one compartment for complexation of alkaline or alkaline earth cations and two compartments for transition-metal cations have been synthesized. The Ba^{2+}-templated (2 + 2) macrocyclization of the dialdehydes **3a** and **3b** with the diamine **8** yielded the barium complexes (**9b**, **9e**) in high yield. The Cs^{+}-templated (2 + 2) macrocyclization of the dialdehyde **3a** and the diamine **8** gave the cesium complex **9c**. The mononuclear complexes were converted into the heterotrinuclear complexes **10a–h** by reaction with 2 equiv of copper, nickel, or zinc acetate. The barium complex **9b**, the dicopper/barium complex **10a**, and the dinickel/barium complex **10b** have been analyzed by X-ray crystallography. In all three crystal structures the O_{10} cavity is folded around the barium cation. The copper–copper distance in the dicopper/barium complex **10a** is 3.50 Å and the nickel–nickel distance in the dinickel/barium complex **10b** is 3.42 Å. The electrochemistry of the copper-containing heterotrinuclear complexes **10a**, **10d**, and **10g** and the nickel-containing heterotrinuclear complexes **10b**, **10e**, and **10h** has been studied by polarography, cyclic voltammetry, and coulometry in DMSO. The dinickel/barium complex **10b** was also studied by Kalousek polarography. The dicopper/metal complexes **10a**, **10d**, and **10g** all show a copper–copper interaction, which is the strongest for the dicopper/barium complex **10a**. Coulometry revealed that the complexes **10a**, **10d**, and **10g** undergo a reduction with two electrons, and cyclic voltammetry showed that the reduction/oxidation processes of **10a**, **10d**, and **10g** are chemically reversible. The reduction/oxidation processes of the nickel-containing heterotrinuclear complexes **10b**, **10e**, and **10h** are complicated by adsorption phenomena. Frozen EPR spectra of **10a** and **10g** exhibit typical triplet spectra with a zero-field splitting of about 0.04 cm^{-1}. This behavior is typical for Cu(II) dimers and confirms that both Cu(II) cations are also exchange coupled in solution. A Cu–Cu distance in solution of 3.6 Å agrees best with the spectra. Attempts to add exogenous bridging ligands like F^- and imidazolate were unsuccessful.

Introduction

The dicopper metalloproteins hemocyanine and tyrosinase contain two Cu(I) metal cations in the active site.[2] The crystal structure of the deoxy state of hemocyanine has been recently published.[3] The two Cu(I) cations are both coordinated by three nitrogen atoms from histidines and the intermetallic distance is about 3.5 Å without a bridging anion. The active site of tyrosinase is similar to that of hemocyanine.[2]

[†] Laboratory of Organic Chemistry, University of Twente.

[‡] Laboratory of Chemical Analysis, University of Twente.

[§] Laboratory of Chemical Physics, University of Twente.

[⊥] Department of Chemistry, Leiden University.

(1) Part of this work has appeared as a preliminary communication: van Veggel, F. C. J. M.; Bos, M.; Harkema, S.; Verboom, W.; Reinhoudt, D. N. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 746.

(2) See for recent reviews of dicopper metalloproteins and synthetic analogues: (a) Latour, J.-M. *Bull. Soc. Chim. Fr.* **1988**, 508. (b) Sorrell, T. N. *Tetrahedron* **1989**, *45*, 3.

(3) (a) Linzen, B.; Soeter, N. M.; Riggs, A. F.; Schneider, H.-J.; Schartau, W.; Moore, M. D.; Yokota, E.; Behrens, P. Q.; Nakashima, H.; Takagi, T.; Nemoto, J. M.; Verijken, J. M.; Bak, H. B.; Beintena, J. J.; Volbeda, A.; Gaykema, W. P. J.; Hol, W. G. J. *Science (Washington D.C.)* **1985**, *229*, 519. (b) Volbeda, A.; Hol, W. G. J. *J. Mol. Biol.* **1989**, *209*, 249.