are slightly shorter than the P(2)–C(1) bond [1.767 (4) Å] to the coordinated P(O) group, indicating more delocalization within the chelate ring.

The Rh–COD bonding is normal. The four Rh–C distances average 2.116 Å in 1 compared to 2.103 Å in (COD)Rh(acac)[32] and 2.118 Å in (COD)Rh[PhC(O)CHC(O)CF3].[33] The olefinic bonds, 1.393 (5) and 1.387 (3) Å, are longer than the 1.341-Å distance in the free COD molecule[34] and only marginally shorter than in (COD)Rh(acac) (mean 1.405 Å)[32] and (COD)Rh[PhC(O)CHC(O)CF$_3$] (mean 1.402 Å).[33] The mean COD (C(sp^2)–C(sp^3) distance in 1 is 1.490 Å, and the mean C(sp^3)–C(sp^3) distance is 1.526 Å, which are well within the expected values.

Acknowledgment. We thank Professors R. H. Crabtree and D. L. Reger for preprints of their manuscripts and helpful discussion and Prof. L. F. Dahl for furnishing X-ray facilities.

Supplementary Material Available: Tables S-I through S-V, listing bond lengths, bond angles, anisotropic displacement coefficients, hydrogen-atom coordinates, and equations for least-squares planes (5 pages); Table S-VI, listing structure factors (15 pages). Ordering information is given on any current masthead page.

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Class II Mixed-Valent Complexes from Oxidation of Doubly Linked (Arene)chromium Compounds

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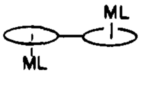
Oxidation of bridged d^6–d^6 dinuclear (arene)chromium complexes having a second linkage of P$_2$Me$_4$ has been studied by electrochemistry and by IR and ESR spectroscopies. Cyclic voltammetry shows that both (biphenyl)[Cr(CO)$_2$]$_2$(μ-P$_2$Me$_4$) (VII) and (diphenylmethane)[Cr(CO)$_2$]$_2$(μ-P$_2$Me$_4$) (VIII) undergo two separate reversible one-electron oxidations in CH$_2$Cl$_2$, with E°'s (vs SCE) of +0.32 and +0.69 V (for VII) and +0.23 and +0.52 V (for VIII). A third complex, (diphenylmethane)[Cr(CO)$_3$]$_2$, has a two-electron oxidation wave for which wave-shape analysis yields E° values of +0.845 and +0.890 V. The monocations of VII and VIII were studied at 263 K by IR spectroscopy and shown to have separate Cr(I) and Cr(0) sites. A similar conclusion was drawn from the frozen-solution ESR spectrum of VIII$^+$. These ion are formulated as class II mixed-valent species in the Robin–Day classification scheme. The IR spectrum of {(biphenyl)[Cr(CO)$_2$PPh$_3$]$_2$}$^+$ was reinvestigated (see ref 16) at 203 K, and a spectrum similar to those of VII$^+$ and VIII$^+$ was obtained. All three class II mixed-valent cations showed carbonyl IR shifts for the Cr(0) site in the range 11–20 cm^{-1} as compared with the neutral starting materials. The structures of VII and VIII were crystallographically determined. For VII, crystal data are as follows: C$_{20}$H$_{22}$Cr$_2$O$_4$P$_2$, monoclinic, $P2_1/n$, a = 13.489 (4) Å, b = 11.800 (3) Å, c = 13.726 (3) Å, β = 107.22 (3)°, V = 2086.79 (11) Å^3, Z = 4, $R(F)$ = 4.09%. The biphenyl ligand is twisted 25.7° to accommodate the gauche conformation of the tetramethyldiphosphine group. A large Cr–Cr separation [4.773 (1) Å] appears to preclude a strong metal–metal interaction. For VIII, crystal data are as follows: C$_{21}$H$_{24}$Cr$_2$O$_4$P$_2$, monoclinic, $C2/c$, a = 14.580 (3) Å, b = 10.359 (3) Å, c = 14.705 (4) Å, β = 108.56 (2)°, V = 2165 (1) Å^3, Z = 4, $R(F)$ = 2.90%.

Introduction

The electronic delocalization properties of mixed-valent dinuclear complexes linked by two carbocyclic ligands continue to be of interest, in part because of the relevance of these models to studies of conducting organometallic polymers.[1-4] Relatively few such complexes have metals on the same face of a bridging hydrocarbon in a syn arrangement (structure IB). Owing to steric repulsions, syn complexes are generally disfavored with respect to the anti isomers (structure IA), and a second linkage is required (IC) to block rotation to the anti orientation. Ions resulting from oxidation of doubly linked systems (IC) form an important class of mixed-valent complexes in that they usually have a highly delocalized electronic structure when the linkages are cyclopentadienyl rings with intervening CY groups [Y = C[5,6] or H(Me)[7] (II, III)] or fulvalene itself[8]



IA

IB

IC

[†] University of Vermont.
[‡] University of Idaho.
[§] University of Delaware.
[∥] University of New Hampshire.

(1) Cowan, D. O.; LeVanda, C.; Park, J.; Kaufman, F. *Acc. Chem. Res.* 1973, *6*, 1.

(2) See: Sheats, J. E., Carraher, C. E., Jr., Pittman, C. U., Jr., Eds.; *Metal-Containing Polymeric Systems*; Plenum Press: New York, 1983. See especially: Simionescu, C.; Lixandru, T.; Tataru, L.; Mazilu, I.; Vata, M.; Scutaru, D.; pp 69–81. Yasuda, H.; Noda, I.; Morita, Y.; Nakamura, H.; Miyanaga, S.; Nakamura, A.; pp 275–290. Bitterwolf, T. E.; pp 137–147.

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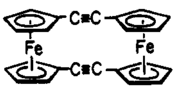
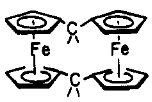
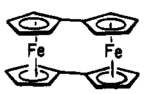
0276-7333/91/2310-2403$02.50/0



II



III

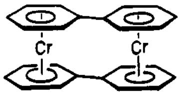


IV

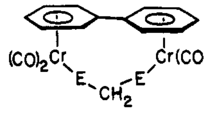
(IV). The monocations derived from II–IV are all formally d^5–d^6 systems. The monocationic dicobalt analogue of IV, bis(fulvalene)dicobalt(1+), represents a formal d^6–d^7 system.[9] It also exhibits electronic delocalization.[10,11]

There is significant controversy over whether delocalization in these doubly linked systems arises from bridge-mediated electron exchange[5,12] or from a direct metal–metal interaction.[6,7,13] The Fe–Fe distance of 3.98 Å in the bis(fulvalene)diiron monocation (IV^+) is strongly suggestive of a through-space M–M interaction,[13b] but the reported delocalization in III^+[7] is harder to explain on that basis.

Dinuclear complexes with a biphenyl linkage may aid in understanding the delocalization mechanism in these systems, since the metal–metal separation is larger by ca. 0.4 Å for two *syn*-metals π-bonded to the centers of a C_6–C_6 linkage as compared to a C_5–C_5 linkage. Indeed, the bis(biphenyl)dichromium cation V^+ is reported to exhibit *localized* mixed valency, at least in frozen media.[14] However, we recently reported that the oxidation of VI, in which the linkages are biphenyl and either bis(diphenylphosphino)methane or -arsino)methane, gives a cation classified as class III mixed valent[15] (totally delocalized) on the basis of electrochemical, IR, and ESR data.[16]



V

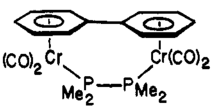


VI, E=PR2,AsR2

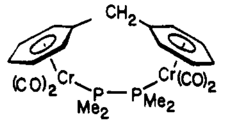
Table I. Crystallographic Parameters for (η^6:η^6-C_6H_5–C_6H_5)$Cr_2(CO)_2$(μ-P_2Me_4) (VII)

	(a) Crystal Parameters		
formula	$C_{20}H_{22}Cr_2O_4P_2$	υ, Å^3	2086.79 (11)
fw	492.35	Z	4
space group	$P2_1/n$	cryst dimens, mm	0.27 × 0.30 × 0.30
cryst syst	monoclinic		
a, Å	13.489 (4)	cryst color	amber
b, Å	11.800 (3)	D(calc), g/cm^3	1.567
c, Å	13.726 (3)	μ(Mo Kα), cm^{-1}	11.90
β, deg	107.22 (3)	temp, °C	23
	(b) Data Collection		
diffractometer	Nicolet R3m	no. of rflns collcd	4035
monochromator	graphite	no. of indpt rflns	3666
scan technique	Ω	R(merg), %	2.05
radiation (λ, Å)	Mo Kα (0.710 73)	no. of indpt rflns obsd (5σ(F_o)	3107
2θ scan range, deg	4–50	std rflns	3 std/197 rflns
		var in stds, %	<1
data collcd	±h,k,l		
	(c) Refinement		
$R(F)$, %	4.09	$\Delta(\rho)$, eÅ^{-3}	0.34
$R_w(F)$, %	3.69	N_o/N_v	12.2
Δ/σ(max)	0.07	GOF	1.352

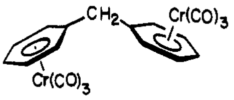
We now report further examples of doubly linked complexes similar to VI. In VII and VIII one linkage is tetramethyldiphosphine and the other is either biphenyl (VII) or diphenylmethane (VIII). The singly bridged diphenylmethane complex IX is included for the purpose of comparison with VIII. Infrared and ESR data on complexes VII^+ and $VIII^+$ indicate that the monooxidized forms should be classified as class II mixed-valent species, exhibiting weak electronic delocalization. In the course of these studies we had cause to reinvestigate the IR spectrum of the monocation derived from (biphenyl)[Cr($CO)_2PPh_3]_2$ (X) reported earlier in ref 16. New results were obtained for X^+ with IR spectral parameters very similar to those of VII^+ and $VIII^+$.



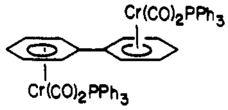
VII



VIII



IX



X

Experimental Section

Complexes. The following compounds were prepared according to published procedures: (biphenyl)[Cr$(CO)_2]_2$(μ-P_2Me_4) (VII);[17a] (diphenylmethane)[Cr$(CO)_3]_2$ (IX);[17b] (biphenyl)[Cr($CO)_2PPh_3]_2$ (X);[17c] Ni[$S_2C_2(CF_3)_2]_2$.[17d] Decamethylferrocene was used as received from Strem Chemicals.

Preparation of (Diphenylmethane)[Cr$(CO)_2]_2$(μ-P_2Me_4) (VIII). A 1.00-g (2.27-mmol) amount of IX in 250-mL of benzene was added under N_2 to an Ace-Hanovia quartz reaction vessel, whereupon P_2Me_4, 0.277 g (2.27 mmol), was added by syringe. The mixture was photolyzed for 24 h, after which the solvent was removed and the resulting red oil was taken up in dichloromethane and filtered through Florisil. The solution was evaporated, and the residue was recrystallized twice from CH_2Cl_2/pentane to give yellow-orange crystals, yield 90 mg, 8%. Carbonyl IR in CH_2Cl_2:

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(12) (a) LeVanda, C.; Bechgaard, K.; Cowan, D. O.; Mueller-Westerhoff, U. T.; Eilbracht, P.; Candela, G. A.; Collins, R. L. *J. Am. Chem. Soc.* **1976**, *98*, 3181. (b) Mueller-Westerhoff, U. T.; Eilbracht, P. *Tetrahedron Lett.* **1973**, 1855. (c) Cowan, D. O.; LeVanda, C.; Collins, R. L.; Candela, G. A.; Mueller-Westerhoff, U. T.; Eilbracht, P. *J. Chem. Soc., Chem. Commun.* **1973**, 329. (d) Kirchner, R. F.; Loew, G. H.; Mueller-Westerhoff, U. T. *Inorg. Chem.* **1976**, *15*, 2665.

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Table II. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³) for (η^6:η^6-C_6H_5–C_6H_5)$Cr_2(CO)_2(\mu$-P_2Me_4) (VII)

	x	*y*	*z*	*U*[a]
Cr(1)	3443 (1)	3327 (1)	−1314 (1)	30 (1)
Cr(2)	2417 (1)	707 (1)	855 (1)	32 (1)
P(1)	2688 (1)	3754 (1)	−68 (1)	35 (1)
P(2)	1663 (1)	2411 (1)	258 (1)	38 (1)
C(1)	3649 (2)	4641 (3)	−1422 (2)	40 (1)
O(1)	3772 (2)	5805 (2)	−1519 (2)	61 (1)
C(2)	2185 (3)	3520 (3)	−2263 (3)	40 (1)
O(2)	1393 (2)	3658 (3)	−2884 (2)	64 (1)
C(3)	2906 (3)	1290 (3)	2138 (3)	45 (1)
O(3)	3193 (2)	1615 (3)	2974 (2)	76 (1)
C(4)	1236 (3)	437 (3)	1184 (3)	41 (1)
O(4)	479 (2)	277 (2)	1413 (2)	63 (1)
C(5)	611 (3)	2396 (3)	−935 (3)	64 (2)
C(6)	1032 (3)	3133 (3)	1099 (3)	76 (2)
C(7)	3519 (3)	4026 (3)	1226 (3)	55 (2)
C(8)	1874 (3)	5034 (3)	−307 (3)	60 (2)
C(11)	4014 (3)	2323 (3)	−2362 (3)	44 (1)
C(12)	4800 (3)	3055 (3)	−1827 (3)	46 (1)
C(13)	5132 (2)	3018 (3)	−758 (3)	42 (1)
C(14)	5132 (2)	3018 (3)	−758 (3)	42 (1)
C(14)	4651 (2)	2300 (3)	−234 (2)	35 (1)
C(15)	3849 (2)	1539 (3)	−760 (2)	30 (1)
C(16)	3554 (3)	1567 (3)	−1834 (2)	36 (1)
C(21)	2420 (3)	177 (3)	−687 (2)	38 (1)
C(22)	3406 (2)	682 (3)	−224 (2)	32 (1)
C(23)	3990 (3)	274 (3)	735 (3)	41 (1)
C(24)	3607 (3)	−600 (3)	1221 (3)	51 (2)
C(25)	2663 (3)	−1102 (3)	745 (3)	55 (2)
C(26)	2070 (3)	−723 (3)	−223 (3)	50 (1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Selected Bond Distances and Angles for (η^6:η^6-C_6H_5–C_6H_5)$Cr_2(CO)_2(\mu$-P_2Me_4) (VII)

(a) Bond Distances (Å)

Cr(1)···Cr(2)	4.773 (1)	P(1)–P(2)	2.234 (1)
Cr(1)–P(1)	2.291 (1)	Cr–C(1,4)$_{av}$	1.818 (4)
Cr(2)–P(2)	2.292 (1)	C–O$_{av}$	1.165 (6)
Cr(1)–CNT(1)	1.701 (2)	C(15)–C(22)	1.477 (5)
Cr(2)–CNT(2)	1.709 (2)		

(b) Bond Angles (deg)

CNT(1)–Cr(1)–P(1)	127.8 (1)	P(1)–Cr(1)–C(2)	88.9 (1)
CNT(1)–Cr(1)–C(1)	125.2 (1)	C(1)–Cr(1)–C(2)	87.2 (1)
CNT(1)–Cr(1)–C(2)	127.1 (2)	P(2)–Cr(2)–C(3)	90.5 (1)
CNT(2)–Cr(2)–P(2)	127.8 (1)	P(2)–Cr(2)–C(4)	85.0 (1)
CNT(2)–Cr(2)–C(3)	127.9 (2)	C(3)–Cr(2)–C(4)	85.4 (2)
CNT(2)–Cr(2)–C(4)	126.2 (2)	Cr(1)–P(1)–P(2)	115.6 (1)
P(1)–Cr(1)–C(1)	87.5 (1)	Cr(2)–P(2)–P(1)	117.3 (1)

(c) Torsion Angles (deg)

Cr(1)–P(1)–P(2)–Cr(2)	62.3 (1)
CNT(1)–C(15)–C(22)–CNT	−9.7 (2)
CNT(1)–Cr(1)–Cr(2)–CNT(2)	−22.4 (1)

Table IV. Crystallographic Data for (Diphenylmethane)[$Cr(CO)_2]_2(\mu$-P_2Me_4) (VIII)

(a) Crystal Parameters

formula	$C_{21}H_{24}Cr_2O_4P_2$	*Z*	4
fw	506.33	cryst dimens, mm	0.30 × 0.30 × 0.30
cryst syst	monoclinic		
space group	*C*2/*c*	cryst color	red
a, Å	14.580 (3)	*D*(calc), g cm^{-3}	1.553
b, Å	10.359 (3)	μ(Mo Kα), cm^{-1}	11.82
c, Å	14.705 (4)	temp, K	295
β, deg	108.56 (2)	*T*(max)/*T*(min)	1.05
V, Å^3	2165 (1)		

(b) Data Collection

diffractometer	Nicolet R3m	no. of indpt rflns	1843
monochromator	graphite	*R*(merg), %	1.92
radiation (λ, Å)	Mo Kα (0.710 73)	no. of indpt obsvd rflns $F_o \geq 4\sigma(F_o)$	1604
2θ scan range, deg	4–50	std rflns	3 std/97 rflns
		var in stds	<1%
data collcd	±*h*,+*k*,+*l*		
no. of rflns collcd	2037		

(c) Refinement

R(*F*), %	2.90	$\Delta(\rho)$, e Å^{-3}	0.38
$R_w(F)$, %	3.48	N_o/N_v	9.12
Δ/σ(max)	0.011	GOF	1.142

Table V. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³) for VIII

	x	*y*	*z*	*U*[a]
Cr	3929.4 (2)	2575.8 (3)	3410.9 (3)	26.6 (1)
P	4733.1 (4)	769.3 (5)	3138.4 (4)	25.3 (2)
C(1)	3083 (2)	2472 (2)	2193 (2)	31 (1)
O(1)	2513 (1)	2388 (2)	1431 (1)	46 (1)
C(2)	3058 (2)	1568 (3)	3741 (2)	38 (1)
O(2)	2471 (1)	988 (2)	3945 (2)	61 (1)
C(3)	4707 (2)	4425 (2)	3260 (2)	31 (1)
C(4)	3802 (2)	4678 (3)	3389 (2)	37 (1)
C(5)	3576 (2)	4219 (3)	4178 (2)	44 (1)
C(6)	4241 (2)	3439 (2)	4850 (2)	44 (1)
C(7)	5120 (2)	3126 (3)	4723 (2)	40 (1)
C(8)	5343 (2)	3618 (2)	3922 (2)	35 (1)
C(9)	5000	5132 (4)	2500	46 (2)
C(10)	4053 (2)	−745 (3)	2995 (2)	41 (1)
C(11)	5841 (2)	285 (3)	4081 (2)	38 (1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

1879 and 1819 cm^{-1}. ^{1}H NMR in C_6D_6 (δ): 5.04 (d, 4 H), 4.73 (t, 2 H), 4.12 (t, 4 H), 2.93 (s, 2 H), 1.20 (s, 12 H). ^{31}P NMR in C_6D_6: 51.30 ppm vs phosphoric acid. Anal. Found (calcd for $C_{21}H_{24}Cr_2O_4P_2$): C, 49.87 (49.80); H, 4.78 (4.74).

Electrochemistry. Procedures were as given earlier.[16] For consistency with the previous paper, potentials are reported versus the aqueous saturated calomel electrode. Conversion to the ferrocene scale requires addition of *minus* 0.46 V. Electrochemical measurements were all made with CH_2Cl_2/0.1 M Bu_4NPF_6 electrolyte. Pt electrodes were employed throughout.

Spectroscopy of Cations. Chemical oxidations and spectroscopic procedures were, with one exception, as reported earlier and employed ferrocenium ion as the oxidant.[16] The IR spectrum of X$^+$ was obtained with bis(*cis*-1,2-(trifluoromethyl)ethylene-1,2-dithiolato)nickel as the oxidizing agent.[17d] Simulations of the IR spectra were performed with a program (DNMR4: Bushweller, C. H.; Letendre, L. J.; Brunelle, J. A.; Bilofsky, H. S.; Whalon, M. R.; Fleischman, S. H. *Quantum Chemistry Program Exchange*; Indiana University: Bloomington, IN, 1983; Program 466) employing Lorentian line shapes for absorbing species. The band positions, integrated intensities, and line widths were changed by alteration respectively of the program's chemical shifts, populations, and relaxation times.

X-ray Crystallography. Crystals of VII and VIII were grown from benzene/pentane solutions. Crystallographic data on VII are collected in Table I. Systematic absences in the diffraction data uniquely determined the monoclinic space group, *P*2$_1$/*n*. No correction for absorption was required (T_{min}/T_{max} = 0.91).

The Cr atoms for both VII and VIII were located by direct methods. All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were treated as idealized isotropic contributions. All software is contained in the SHELXTL (5.1) program library (G. Sheldrick, Nicolet XRD, Madison, WI). Atomic coordinates for VII are given in Table II, and selected bond distances and angles appear in Table III.

Crystallographic data, positional and thermal parameters, and bond distances and angles for VIII are collected in Tables IV–VI. Crystals diffracted strongly with narrow line widths. A specimen mounted on a glass fiber possessed 2/*m* Laue symmetry. Systematic absences defined either of the *C*-centered monoclinic space groups, *Cc* or *C*2/*c*. The latter, centrosymmetric, alternative was initially chosen on the basis of the distribution of *E* statistics and the potential presence of 2-fold rotational symmetry; the chemically reasonable results of refinement in this space group confirmed the choice. The data were empirically corrected for absorption.

Table VI. Selected Bond Distances and Angles for VIII

(a) Bond Distances (Å)

Cr–P	2.310 (1)	Cr–C(7)	2.221 (2)
Cr–C(1)	1.826 (2)	Cr–C(8)	2.235 (2)
Cr–C(2)	1.825 (3)	P–P′	2.250 (1)
Cr–C(3)	2.272 (2)	C(1)–O(1)	1.166 (3)
Cr–C(4)	2.185 (3)	C(2)–O(2)	1.161 (4)
Cr–C(5)	2.192 (3)	Cr–CNT	1.722 (1)
Cr–C(6)	2.207 (3)		

(b) Bond Angles (deg)

CNT–Cr–P	125.6	P–Cr–C(1)	90.2 (1)
CNT–Cr–C(1)	129.3 (2)	P–Cr–C(2)	91.0 (1)
CNT–Cr–C(2)	123.2 (2)	Cr–P–P′	118.3 (0)
C(1)–Cr–C(2)	85.3 (1)	C(3)–C(9)–C(3′)	121.8 (3)

(c) Torsion Angles (deg)

CNT–Cr···Cr′–CNT′	−72.2	[C(3)–C(8)]–[C(3′)–C(8′)]	108.1
Cr–P–P′–Cr′	46.1		

Table VII. Formal Potentials for Oxidation of (Arene)chromium Complexes in This Study and Related Earlier Work[a]

compd	$E°_1$	$E°_2$	$\Delta E°$	ref
(biphenyl)[$Cr(CO)_2]_2(\mu-P_2Me_4)$ (VII)	320	690	370	
(diphenylmethane)[$Cr(CO)_2]_2(\mu-P_2Me_4)$ (VIII)	230	520	290	
(diphenylmethane)[$Cr(CO)_3]_2$ (IX)	845	890	45	
(biphenyl)[$Cr(CO)_3]_2$	800	1000	200	16
(biphenyl)[$Cr(CO)_2(PPh_3)]_2$ (X)	260	520	260	16
(biphenyl)[$Cr(CO)_2]_2$(μ-dppm) (VI)	100	640	540	16
(biphenyl)[$Cr(CO)_2]_2$(μ-dmpm)	40	590	550	16

[a] See ref 16 for earlier work. Potentials are in millivolts vs SCE. The electrolyte is CH_2Cl_2/0.1 M Bu_4NPF_6.

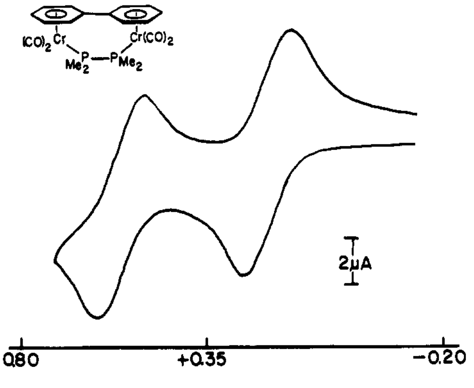

Figure 1. Cyclic voltammogram at a Pt electrode of 2 × 10^{-4} M VII in CH_2Cl_2 at 298 K. Scan rate = 0.20 V/s.

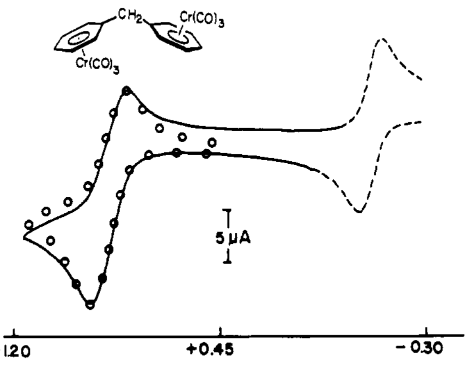

Figure 2. Cyclic voltammogram of 5 × 10^{-4} M IX and equimolar Cp^*_2Fe in CH_2Cl_2 at a Pt electrode at 298 K. Scan rate = 0.20 V/s; circles give results of simulation with $E°$ values of +0.845 and +0.890 V.

Results and Discussion

Electrochemistry. The two tetramethyldiphosphino-bridged complexes VII and VIII display two reversible oxidations in CH_2Cl_2 (eqs 1 and 2), with formal potentials

$$\text{VII (or VIII)} \rightleftharpoons \text{VII}^+ \text{ (or VIII}^+) + e^- \quad (1)$$

$$\text{VII}^+ \text{ (or VIII}^+) \rightleftharpoons \text{VII}^{2+} \text{ (or VIII}^{2+}) + e^- \quad (2)$$

given in Table VII. The chemical reversibility of the couple $VIII^+/VIII^{2+}$ was quite limited, requiring CV sweep rates of >10 V/s to outrun a decomposition reaction at 298 K.[18] With that exception, the voltammetry was straightforward (Figure 1). Waves were diffusion-controlled. Diagnostic criteria were appropriate for essentially Nernstian charge-transfer processes.[19]

Bulk coulometry was performed on 0.7 mM VII in a vacuum cell at room temperature. With E_{appl} = 0.50 V (first oxidation) the solution went from yellow to maroon, with 0.97 F passed after 95% completion of the electrolysis. Some precipitation of the monocation was noticed. The precipitate dissolved, and the neutral complex was regenerated by subsequent application of E_{appl} = 0 V.

The monocation of VII was also prepared by oxidation with equimolar Cp_2Fe^+. The reaction was monitored in an electrochemical cell with a rotating Pt electrode. VII^+ exhibited a half-life of approximately 1 h at 298 K under these conditions, the decomposition product being the starting material VII. With a 0.5 mM solution, no insoluble product was noted at 298 K, but a maroon precipitate formed at 273 K. Bulk coulometry was not performed on VIII, but oxidation of the complex by Cp_2Fe^+ was followed by rotating Pt electrode voltammetry. The monocation $VIII^+$ was soluble under these conditions and had a half-life of ca. 0.5 h.

Complex IX gave considerably different electrochemical characteristics. A single wave was observed with $E°_{appl}$ = 0.87 V. The shift to a potential higher than that of VII arises from the substitution of CO for PR_3 in the $Cr(CO)_2L$ moiety. Apparently, only one wave is observed because the two one-electron oxidations of IX are unresolved. The current function for this wave was 1.75 times that of equimolar decamethylferrocene,[20] consistent with this interpretation. The breadth of the wave ($E_p - E_p/2$) was 86 mV, rather than the 57 mV predicted for a Nernstian one-electron process.[21]

Peak breadths may be used to estimate the formal potentials of EE systems[22] in which the $E°$ values are very close.[23] However, simulation of the entire wave is a more rigorous approach. Consequently, we performed digital simulations matching the CV curve of IX with a scan rate of 0.2 V/s. Good agreement with experiment was found (Figure 2) with $E°_1$ = 0.845 V and $E°_2$ = 0.890 V (Table VII), a separation of 45 mV in formal potentials for the

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(18) Many papers have been written on the subject of the chemical reversibility of (η^6-arene)$Cr(CO)_2L$ oxidations. For leading references, see: Stone, N.; Sweigart, D. A.; Bond, A. M. *Organometallics* **1986**, *5*, 2553. Dr. Allen Hunter (University of Alberta), personal communication to W.E.G., has shown that these systems exhibit greater chemical reversibility when activated alumina is present in the electrochemical cell, an observation that we have confirmed.

(19) For example, for VII/VII^+ with scan rate = 0.05 V/s, $E_p - E_p/2$ = 59 mV, ΔE_p = 67 mV, $E_p - E°$ = 28 mV, and i_c/i_a = 1.0. The ΔE_p values were compared to those of $Cp_2Co^{+/0}$ over the scan rate range 0.02–0.60 V/s and found to be higher by 3–20 mV.

(20) Decamethylferrocene was employed as a one-electron internal standard for this series of complexes in order to avoid overlap of the (arene)$Cr(CO)_3$ waves with that of ferrocene.

(21) That the greater peak breadth was not due to slow heterogeneous charge-transfer kinetics or solution resistance was shown by its invariance with sweep rate.

(22) EE systems are those in which a molecule undergoes consecutive one-electron transfers without the intermediacy of a chemical reaction.

(23) (a) Richardson, D. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 1278. (b) Myers, R. L.; Shain, I. *Anal. Chem.* **1969**, *41*, 980.

couples $IX^{0/+}$ and $IX^{+/2+}$. Complete chemical reversibility of this wave was only observed with scan rates above 0.2 V/s.

The CV study of IX was complicated by electrode fouling, and the electrode (either Pt or Au) required wiping after each scan. This problem was particularly severe at subambient temperatures, and classic stripping peaks were seen in the cathodic portion of the scans, owing to the presence of insoluble dication on the electrode surface.

We will now consider what information about electronic delocalization can be obtained from the $\Delta E°$ values of VII–IX, where $\Delta E° = E°_2 - E°_1$. It has been established that two noninteracting redox centers (class I mixed valent) have a $\Delta E°$ value of about 36 mV.[24] On the other hand, class III (totally delocalized) systems generally have larger $\Delta E°$ values.[25] For example, $E°_2 - E°_1$ = 540 mV for the delocalized doubly linked system $VI/VI^+/VI^{2+}$.[16]

The value of $\Delta E°$ = 45 mV for IX is consistent with at best a very weak interaction between the two redox centers. Since some of the broadening of the experimental wave of IX may arise from uncompensated resistance effects and/or non-Nernstian charge-transfer processes, we consider the calculated $\Delta E°$ of 45 mV to be within experimental error of that expected for noninteracting oxidation centers. The dicyclopentadienylmethane analogue, $CpFe(C_5H_4CH_2C_5H_4)FeCp$, has a larger value, 170 mV.[13c,26] Although no spectroscopic data were obtained on the cation(s) of IX, we expect that this diphenylmethane singly linked complex has localized oxidation sites, going successively from Cr^0Cr^0 to Cr^ICr^0 to Cr^ICr^I.

The $\Delta E°$ values are considerably larger for the doubly linked systems VII (370 mV) and VIII (290 mV) than they are for IX. These values are in the range reported for biferrocene,[27] a singly linked system that exhibits class II mixed-valent behavior.[28]

Spectroscopic Studies of Monocations. Infrared Spectra. Infrared spectra of the monocations of VII and VIII should provide the most direct indication of electronic delocalization on a short time scale. The monocation VI^+ had a pair of bands in the CO-stretching region shifted an average of 75 cm^{-1} to higher energy than the neutral complex. This was taken to indicate equivalence of the two metals and a formal $Cr^{0.5}Cr^{0.5}$ oxidation-state description in the delocalized monocation.[16] Mononuclear (arene)-$Cr(CO)_2L$ complexes show shifts in the ν_{sym} band in excess of 100 cm^{-1} for a full Cr^0/Cr^I oxidation.[29] Spectra of VII^+ and $VIII^+$ were obtained by using the flow cell previously described,[16] with equimolar Cp_2Fe^+ as the oxidant. The temperature of the reaction chamber was 248 K, and that of the IR cell was 263 K.[30]

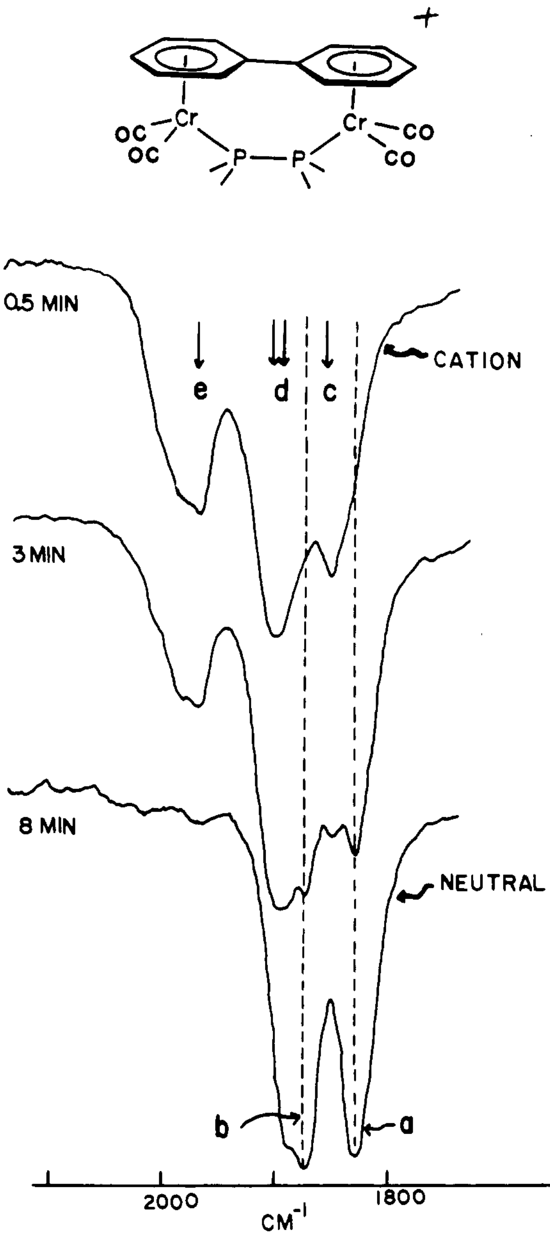

Figure 3. IR spectra of 10^{-3} M VII in CH_3NO_2 at 263 K after reaction with equimolar ferrocenium ion at 248 K: top, spectra accumulated after 30 s at 263 K; middle, spectrum after 180 s; bottom, spectrum after 480 s. The top spectrum is that of VII^+, the bottom that of neutral VII, and the middle that of a mixture of the two.

Table VIII. Carbonyl-Region IR Bands for Pertinent Complexes[a]

compd	ν_{CO}, cm^{-1}
(biphenyl)$[Cr(CO)_2]_2(\mu\text{-}P_2Me_4)$ (VII)[b]	1877, 1830
VII^+[b]	1971, 1898,[c] 1851
(diphenylmethane)$[Cr(CO)_2]_2(\mu\text{-}P_2Me_4)$ (VIII)[b]	1879, 1819
$VIII^+$[b]	1981, 1890,[c] 1834
(biphenyl)$Cr(CO)_2(PPh_3)$[16,a]	1887, 1833
$[(biphenyl)Cr(CO)_2(PPh_3)]^+$[16,a]	1993, 1886
$(Me_6C_6)Cr(CO)_2(PPh_3)$[d,e]	1857, 1796
$[(Me_6C_6)Cr(CO)_2(PPh_3)]^+$[d,e]	1969, 1853

[a] Spectra recorded in CH_3NO_2 except for X and X^+, for which CH_2Cl_2/0.1 M Bu_4NPF_6 was employed. [b] T = 263 K. [c] Broad peak, assigned as composite of ν_{asym} of Cr(I) site and ν_{sym} of Cr(0) site. [d] T = ambient. [e] Data taken from ref 29.

The CO-region IR spectrum of VII^+ is shown in Figure 3. It has more than the two bands expected of a totally delocalized system. Three major absorption bands are

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(24) $\Delta E°$ for two noninteracting redox centers in the same molecule is 35.6 mV and arises from statistical factors; see: (a) Ammar, F.; Saveant, J. M. *J. Electroanal. Chem., Interfacial Electrochem.* 1973, *47*, 215. (b) Flanagan, J. B.; Margel, S.; Bard, A. J.; Anson, F. C. *J. Am. Chem. Soc.* 1978, *100*, 4248.

(25) $\Delta E°$ for the Creutz-Taube system $[(NH_3)_5Ru(pyrazine)Ru(NH_3)_5]^{4+/5+/6+}$ is 390 mV: Creutz, C.; Taube, H. *J. Am. Chem. Soc.* 1973, *95*, 1086.

(26) Shu, P.; Bechgaard, K.; Cowan, D. O. *J. Org. Chem.* 1976, *41*, 1849.

(27) $\Delta E°$ values for biferrocene: 350 mv in CH_2Cl_2;[5] 330 mV in CH_3CN (Morrison, W. H., Jr.; Hendrickson, D. N. *J. Chem. Phys.* 1973, *59*, 380.

(28) For leading references to the many publications on the biferrocenium ion, see: Dong, T.-Y.; Kambara, T.; Hendrickson, D. N. *J. Am. Chem. Soc.* 1986, *108*, 4423.

(29) (a) Connelly, N. G.; Demidowicz, Z.; Kelly, R. L. *J. Chem. Soc., Dalton Trans.* 1975, 2335. (b) Connelly, N. G.; Demidowicz, Z. *J. Organomet. Chem.* 1974, *73*, C31.

(30) Subambient temperatures were employed to ensure the chemical stability of the monocations. Since ferrocenium hexafluorophosphate is poorly soluble in dichloromethane at low temperatures, CH_3NO_2 was used as the oxidation medium, except in the case of X.

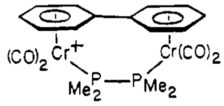
Table IX. Carbonyl IR Shifts (in cm^{-1}) of Dinuclear Trapped-Valence Cations from Assignments in This Study, with Comparison to Shifts Reported Earlier for Oxidation of Mononuclear Complexes

	Cr(I) site		Cr(0) site	
compds compared	ν_{sym}	ν_{asym}	ν_{sym}	ν_{asym}
VII$^+$–VII	94	~68	~21	21
VIII$^+$–VIII	105	~71	~11	15
X$^+$–X	102	58	20	24
(η^6-biphenyl)Cr(CO)$_2$PPh$_3$$^{+,0}$ [16]	106	53	none	
(η^6-C$_6$Me$_6$)Cr(CO)$_2$PPh$_3$$^{+,0}$ [29]	112	57	none	

observed for the monocation (Figure 3, top). The bottom spectrum in Figure 3 was recorded after the solution spent 8 min in the IR cell and shows that neutral VII is regenerated upon standing (bands a and b). The key bands for the monocation are those at 1851 cm^{-1} (band c) and ca. 1971 cm^{-1} [31] (band e). The latter arises from ν_{sym} of a fully oxidized, i.e. Cr(I), site, since the shift is 94 cm^{-1} from the symmetric stretch of the neutral complex. The 1851-cm^{-1} band is only slightly shifted (21 cm^{-1}) from ν_{asym} of the neutral complex and is assigned to an unoxidized, i.e. Cr(0), site, which has been slightly perturbed by the linkage to the Cr(I) site.

The broad third band at 1898 cm^{-1} (band d) must contain ν_{asym} of the Cr(I) site and ν_{sym} for the Cr(0) site, leading to assigned shifts of ca. 68 cm^{-1} for Cr(I) ν_{asym} and ca. 21 cm^{-1} for Cr(0) ν_{sym}. IR band positions are collected in Table VIII, and the energy shifts between the neutral and cationic complexes are given in Table IX.

We conclude that the monocation of VII is valence-trapped on the IR time scale, with separate Cr(I) and Cr(0) sites:



However, some charge donation occurs between the Cr(0) and Cr(I) sites, resulting in a small but measurable (ca. 20 cm^{-1}) shift of the two bands for the Cr(0) carbonyls to higher frequency. This weak interaction may occur through either the P$_2$Me$_4$ or biphenyl linkages (vide infra).

A similar picture emerges from the IR spectrum of VIII$^+$ (Figure 4). ν_{asym} for the Cr(I) site and ν_{sym} for the Cr(0) site again account for the broad band (d) at 1890 cm^{-1}. The calculated shifts for ν_{sym} and ν_{asym} are 102 and ca. 70 cm^{-1}, respectively, for the Cr(I) site, and 11 and 15 cm^{-1} for the Cr(0) site. Thus, both doubly linked systems with P$_2$Me$_4$ bridges display *valence-trapped* vibrational spectra.

A question arises concerning the significance of the ca. 20-cm^{-1} IR shift for the Cr(0) site in VII$^+$ and VIII$^+$, since the cation derived from the singly bridged biphenyl complex X was reported to have *no* measurable shift of the CO frequencies of the Cr(0) site.[16] Since this comparison was important in determining the role of the P$_2$Me$_4$ linkage on the IR shifts, we reinvestigated the spectra of X$^+$ under conditions that were more rigorous than those previously employed. A reassignment of the spectra was found to be necessary.

In our earlier paper[16] we reported spectra of the oxidation product of X at 263 K in CH$_3$NO$_2$ (oxidant: Cp$_2$Fe$^+$) and assigned a band at 1834 cm^{-1} to the Cr(0) site in the mixed-valent cation X$^+$. This band falls at the same energy as ν_{asym} of neutral X. We now report that the 1834-cm^{-1} band apparently arose from regeneration of neutral X in the IR cell. The other bands in that spectrum (ref 16, Figure 4) may be attributed to the mononuclear cation radical, [(biphenyl)Cr(CO)$_2$(PR$_3$)]$^+$ (see ref 16, Table VII). The latter is known to be a decomposition product of X$^+$.

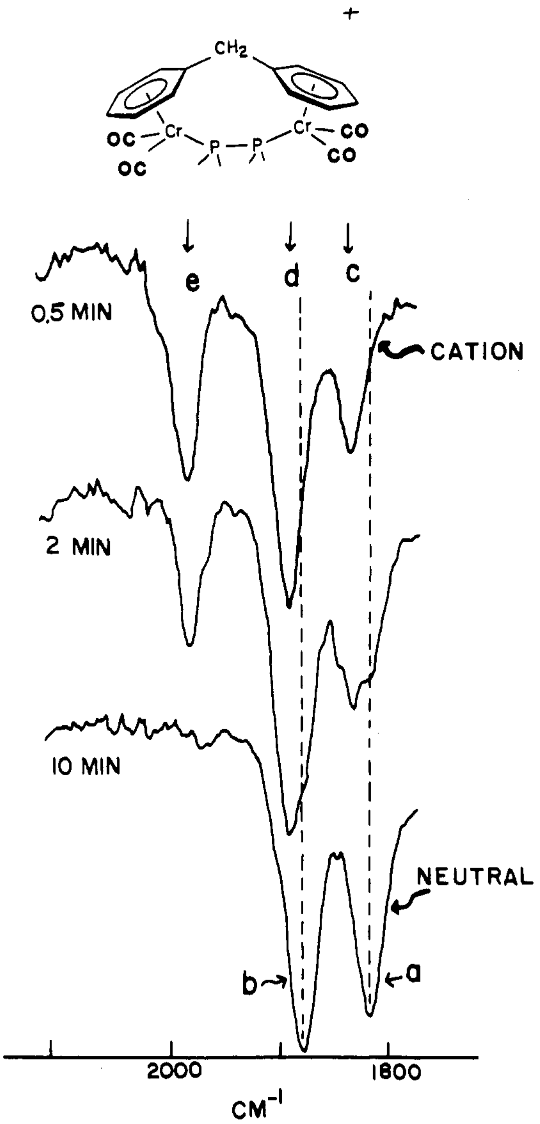


Figure 4. IR spectra of 10^{-3} M VIII$^+$ under the same reaction conditions as those of Figure 3: top, VIII$^+$ after 30 s; bottom, VIII regenerated from VIII$^+$ after 600 s in IR cell; middle, mixture of VIII and VIII$^+$ present after 120 s.

In order to carry out the rapid oxidation of X at lower temperatures, Ni[S$_2$C$_2$(CF$_3$)$_2$]$_2$ was employed as the oxidant. This formal Ni(IV) complex is quite soluble in cold dichloromethane and is easily able to oxidize X, since its Ni(IV)/Ni(III) formal potential is +0.82 V vs SCE,[32] compared to +0.26 V for the couple X$^+$/X^0. Approximately 2 mg of X in a few milliliters of CH$_2$Cl$_2$ was cooled to 208 K, whereupon 1 equiv of the Ni(IV) complex in 2.5 mL of CH$_2$Cl$_2$ at the same temperature was added. After 1 min the dark red solution was drawn into the IR cell, which was thermostated at 203 K. No change of the spectrum was noted over 5 min. Addition of decamethylferrocene to the red solution quantitatively reduced the monocation back to the neutral complex, ensuring that the spectra recorded were not those of decomposition products.

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[31] The band at ca. 1971 cm^{-1} in Figure 3 is not symmetric, but we believe the asymmetry arises from a relatively minor secondary absorption on the high-frequency side.

[32] Geiger, W. E.; Mines, T. E.; Senftleber, F. C. *Inorg. Chem.* **1975**, *14*, 2141.

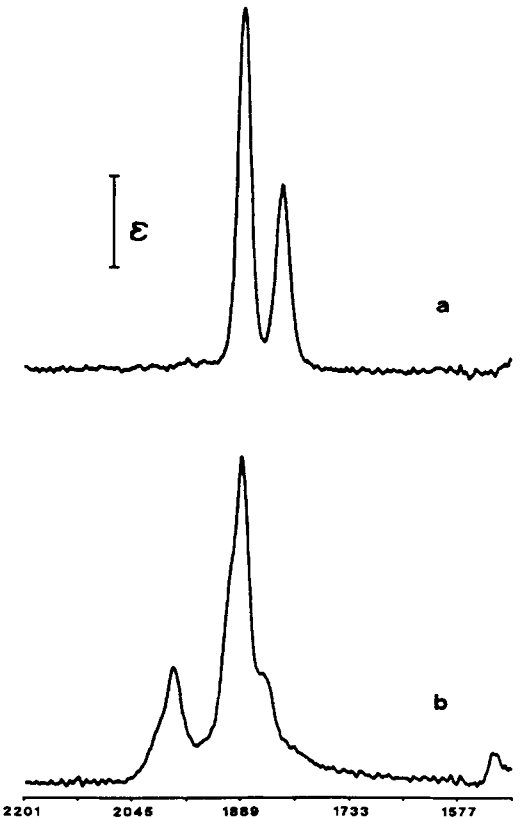

Figure 5. IR spectra in absorbance mode of (a) 0.46 mM X and (b) 0.64 mM X$^+$. Conditions: 203 K in CH_2Cl_2. Spectrum a was obtained after back-reduction of the monocation by $Cp^*{}_2Fe$.

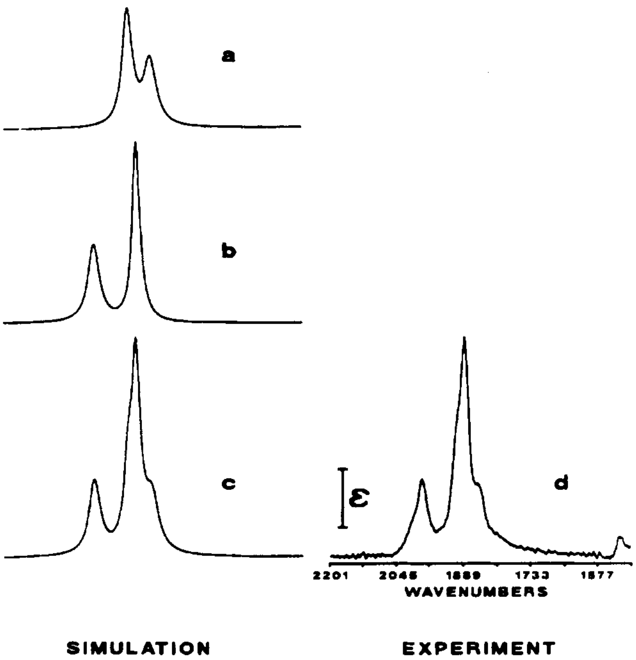

Figure 6. Calculated (left) and observed (right) IR spectra of X$^+$. Doublets a and b are the contributions assigned to the Cr(0) and Cr(I) sites, respectively. Spectrum c at the lower left is the sum of doublets a and b.

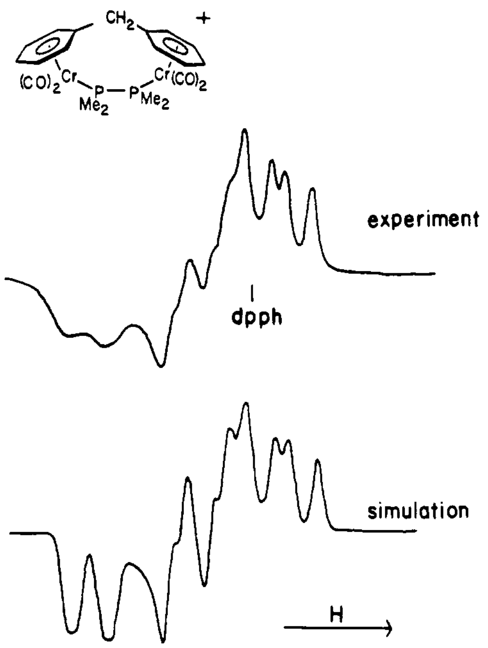

Figure 7. X-Band ESR spectrum of VIII$^+$ in $CH_2Cl_2/C_2H_4Cl_2$ at 77 K (top) and simulated spectrum (bottom) using the parameters in Table X and a uniform line width of 3.9 G.

Table X. ESR Data for Cation Radicals Observed in This Study[a]

complex	g	^{31}P hfs, G
$[(biphenyl)[Cr(CO)_2]_2(\mu\text{-}P_2Me_4)]^+$ (VII$^+$)	2.087	
	2.014	
	1.979	
$[(diphenylmethane)[Cr(CO)_2]_2(\mu\text{-}P_2Me_4)]^+$ (VIII$^+$)	2.087	26.3, 8
	2.036	29.7, 10
	1.996	30.5, 20
$[(biphenyl)Cr(CO)_2(PPh_3)]^+$ [16]	2.103	29.9
	2.034	32.4
	1.992	29.4

[a] Data recorded at $T = 77$ K in $CH_2Cl_2/C_2H_4Cl_2$.

Figure 5 shows the spectra obtained for X (top) and for X$^+$ (bottom). Because the spectrum of the monocation was too complex to analyze by direct measurement, computational fitting was used to deconvolute the overlapping bands. A Lorentzian line shape was assumed. The result is shown in Figure 6. The spectra on the bottom left and bottom right are the calculated and observed results, respectively. Above the calculated spectrum are shown the two pairs of doublets, which add up to give the final calculated result. That at the top (a) is assigned to the Cr(0) site. Below it is (b) the pair of bands shifted to higher energy, assigned to the Cr(I) site. The energies of the four component bands are given in Table VIII. The unambiguous values are those at 1984 cm^{-1}, assigned to the Cr(I) ν_{sym} band, and 1850 cm^{-1}, assigned to the Cr(0) ν_{asym} band. The energy shifts from neutral X, therefore, are 96 cm^{-1} for the former and 16 cm^{-1} for the latter. These values are consistent with those measured for the mixed-valent complexes VII$^+$ and VIII$^+$.

ESR Spectra. ESR spectra of VII$^+$ and VIII$^+$ could only be observed in frozen media.[33] That of VII$^+$ was unusual in that no phosphorus hyperfine splittings were resolved within the spectral line width. The rhombic g tensor of $g_1 = 2.087$, $g_2 = 2.014$, and $g_3 = 1.979$ is as expected for a Cr(I) radical of this type.[16,29] The lack of resolved ^{31}P couplings is unexplained at this point.

Spectra of VIII$^+$ were of higher quality and contained ^{31}P couplings (Figure 7). Simulation of these spectra assuming coincident **g** and **A** tensors gave a best fit with (Table X) $g_1 = 2.087$, $A_{P1} = 26.3$ G, $A_{P'1} = 8.0$ G; $g_2 = 2.036$, $A_{P2} = 29.7$ G, $A_{P'2} = 10.0$ G; and $g_3 = 1.996$, $A_{P3} = 30.5$ G,

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[33] Cations of the type $[(arene)Cr(CO)_2PR_3]^+$ do not appear to give fluid-solution ESR spectra, probably owing to excessively rapid relaxation rates. The data quoted here are in a 1:1 mixture of $CH_2Cl_2/1,2\text{-}C_2H_4Cl_2$ at 77 K following oxidation of the neutral complexes with ferrocenium at 273 K.

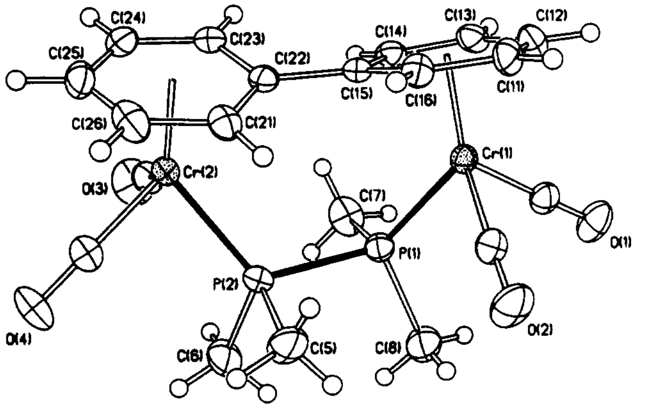

Figure 8. Molecular structure and atom-labeling scheme for VII, (biphenyl)[Cr(CO)$_2$](μ-P$_2$Me$_4$).

$A_{P'3}$ = 20.4 G. Attempts were made to verify these values by recording the Q-band ESR spectra, but these experiments failed owing to sample decomposition. The two inequivalent sets of ^{31}P splittings are consistent with the IR result, which showed that there are Cr(I) and Cr(0) sites in VIII$^+$. The P atom having splittings of 26-30 G in the three principal g directions is the one bonded to the Cr(I) atom, since its hyperfine splittings are similar to those seen for analogous mononuclear radicals[16,29] or trapped-valent dinuclear radicals.[16] The set of smaller ^{31}P splittings is qualitatively consistent with a phosphorus bonded to a Cr(0) site, although no quantitative interpretation is offered at this time.

Structures of VII and VIII. Compound VII crystallizes as discrete molecules without significant intermolecular associations; the molecular structure and atom-labeling scheme are shown in Figure 8. A large metal-metal separation of 4.773 (1) Å precludes a strong Cr–Cr interaction. Each metal atom is approximately octahedrally coordinated in a typical "three-legged piano stool" structure.

Two η^6:η^6-biphenyl complexes, without additional bridges between the metal atoms, have been previously structurally characterized: (η^6:η^6-biphenyl)(Cp*Fe)$_2$[34] and (η^6:η^6-biphenyl)[(CO)$_3$Cr]$_2$.[35] Both are of type IA (anti orientation) with strictly coplanar phenyl rings (In biphenyl itself, the rings are also coplanar[36]). In contrast, the planes of the phenyl rings of complex VII are twisted 27.5°; this may be compared to the much larger twist angle in VI of 50.8°.[16] Neither of the reports of the singly bridged biphenyl complexes contained the central C–C bond distance, which in the free ligand is 1.493 (3) Å.[36] In the doubly bridged complexes it is actually shorter: VI, 1.459 (8) Å; VII, 1.477 (5) Å. Apparently, the barrier to twisting the planes and compressing the central bond is not large and occurs as an accommodation for the ligating demands of the bridging phosphorus ligands. The three-atom, P–C–P, bridge in VI, compared to the two-atom bridge in VII, causes both a greater twist of the rings and a greater compression of the central C–C bond. Figure 9 shows that, as an additional steric accomodation, the P–P and central C–C bonds are not parallel, being offset by 26.4°.

Figure 9 shows both the twisting of the phenyl rings and the gauche conformation of the tetramethyldiphosphine ligand; the Cr–P–P–Cr dihedral angle of 62.3° can be taken as an approximation of the (lone pair)–P–P–(lone pair) dihedral angle. In (μ-Me$_2$PPMe$_2$)[(CO)$_4$Fe]$_2$,[37] the only other dinuclear complex of Me$_2$PPMe$_2$ that has been structurally characterized, the diphosphine is in the trans conformation. The P–P distance in the Fe(CO)$_4$ complex, 2.231 (7) Å, and that in VII, 2.234 (1) Å, are identical and typical of normal P–P single bonds.[38] Thus, of the two bridging groups in VII, it would appear that biphenyl is the more easily distorted.

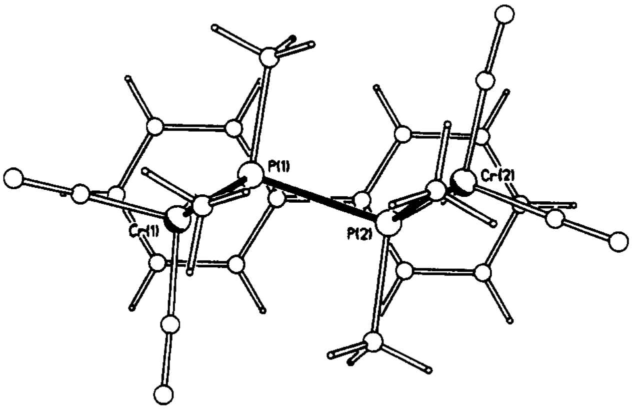

Figure 9. View of VII parallel to the chromium–arene axis.

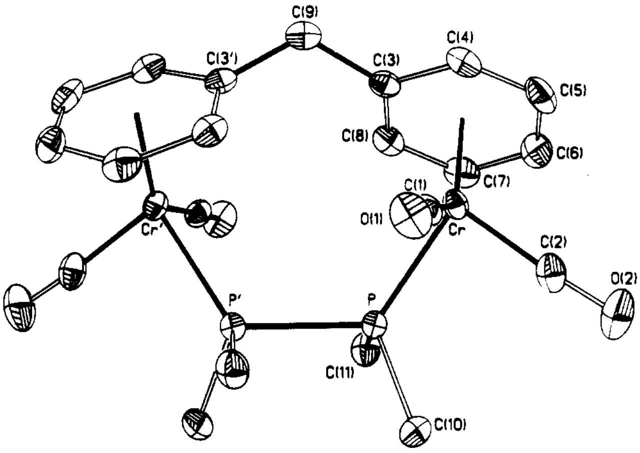

Figure 10. Molecular structure and atom-labeling scheme for VIII, (diphenylmethane)[Cr(CO)$_2$](μ-P$_2$Me$_4$).

The structure of the diphenylmethane-bridged complex VIII is unremarkable. A view of this molecule is shown in Figure 10.

Significance of Results

As mentioned above, doubly linked systems having cyclopentadienyl or substituted cyclopentadienyl linkages have been shown in most cases to exhibit a high degree of delocalization in formally d^5-d^6 complexes.[5-8] Insufficient work under the same conditions has appeared on analogous biphenyl complexes to allow for general conclusions [e.g., *localized* V$^+$ in frozen matrix[14] vs *delocalized* VI$^+$ in fluid matrix]. The present work concludes that two other doubly linked mixed-valent cations of this type also exhibit trapped valence. The observation that the cations of VII$^+$ and VIII$^+$ have nonequivalent Cr(CO)$_2$PPh$_3$ groups dictates against their classification as class III mixed-valent complexes. They are classified as class II, rather than class I, complexes on the basis of their IR spectra, which are not

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mere superpositions of those of isolated Cr(I) and Cr(0) sites. The ca. 10–20-cm^{-1} shift for the carbonyls at the formal Cr(0) site is the key piece of evidence here. The ESR results (two inequivalent ^{31}P splittings for VIII$^+$) and voltammetry results (moderate ΔE° values) offer support for this interpretation.

The 10–20-cm^{-1} CO IR shift may arise from through-bond coupling involving either the Cr–P–P–Cr σ framework or the biphenyl linkage. There is precedent for this magnitude of shift in redox studies of heterobimetallic metal carbonyl complexes with inherently different redox sites. Examples include tricobalt clusters with an attached ferrocene,[39] Mo(CO)$_4$(PR$_2$)$_2$ linked to bis(arene)chromium,[40] and Re(CO)$_3$ with a coordinated benzoylpyridine,[41] all of which showed ν_{sym}(CO) shifts of 12–24 cm^{-1} even though the M(CO)$_x$ moiety was not formally involved in the redox process.

Why is the dppm-bridged complex VI$^+$ a class III mixed-valent complex (totally delocalized) whereas the tetramethyldiphosphino-bridged complex VII$^+$ is a class II species? This question cannot be answered with confidence without knowledge of the structure of the monocation of VII. Our previous work[16] showed that significant structural changes may occur upon oxidation of this general class of compounds. Unfortunately, the slow regeneration of VII from VII$^+$ has precluded success in efforts to grow crystals of the cation suitable for X-ray analysis. We are left, then, to briefly consider some of the possibilities.

In earlier work we noted that the dihedral angle of the biphenyl group in VI$^+$ was only 3°, as opposed to 50° in neutral VI,[16] and implied that the delocalization of VI$^+$ arose from interactions across the (almost coplanar) biphenyl bridge. It is possible that the shorter P$_2$ bridge in VII imparts greater rigidity to the complex and does not allow a significant structural rearrangement in the monocation. This would leave the biphenyl group in a twisted configuration (25.7° in neutral VII) and cut down on the possibility of electron transfer through the π system.[42]

We should, however, also consider the possibility of through-space interactions arising from direct M–M orbital overlap. The Cr–Cr distance in neutral VII is 4.773 Å, which may be compared to 4.828 Å in VI and 4.374 Å in VI$^+$. It is difficult to specify the maximum M–M distance that could give rise to the type of delocalization being considered here, so it is quite possible that the delocalization of VI$^+$ arises from a through-space metal–metal interaction. Without a crystal structure of VII$^+$ it is not possible to say whether the poorer delocalization in the P$_2$Me$_4$ complexes arises from a larger metal–metal distance or a twisted biphenyl system. The question of M–M delocalization vs ligand-bridged delocalization in these systems remains open to debate and is the subject of ongoing studies with systems that are geometrically rigid.

Note Added in Proof. A recent paper on the dication of (biphenyl)bis[(benzene)chromium] is relevant to this work: Elschenbroich, C.; Heck, J.; Massa, W.; Birkhahn, M. *Chem. Ber.* **1990**, *123*, 2321.

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Supplementary Material Available: Tables of bond lengths, bond angles, anisotropic thermal parameters, and hydrogen positional and thermal parameters (4 pages); a table of structure factors (19 pages). Ordering information is given on any current masthead page.

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Synthesis and Electrophilic Destannylation Reactions of Trimethylstannyl-Substituted Methyl Crotonates

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Four methyl(trimethylstannyl)crotonates have been prepared. Methyl (*E*)-2-(trimethylstannyl)crotonate and methyl (*E*)-3-(trimethylstannyl)crotonate were obtained from the Pd(0)-catalyzed hydrostannation of methyl-2-butynoate. Methyl (*Z*)-2-(trimethylstannyl)crotonate and methyl (*Z*)-3-(trimethylstannyl)crotonate were obtained from the AIBN-catalyzed hydrostannation of the same alkynoic ester. Structures were confirmed by ^{1}H and ^{13}C NMR spectra. Reactivity in protodestannylation was determined from kinetic studies and the stereochemistry of the reaction determined by deuteriodestannylation. The 2-trimethylstannyl derivatives react by the allenol mechanism, while the 3-trimethylstannyl derivatives react by the normal S$_E$2 mechanism. Bromodestannylation of the four isomers is accomplished with retention of configuration. Methyl (*Z*)-3-(trimethylstannyl)crotonate is the least reactive to electrophilic destannylation, and methyl cleavage from tin is competitive with vinyl cleavage for reaction with both acid and bromine.

Introduction

In recent years the chemistry of vinylstannanes has received considerable interest from the standpoint of both synthesis and reactions. Hydrostannation of alkynes, when catalyzed by transition metals, results in good control of both the regiochemistry and stereochemistry of addition for a number of functionally substituted internal and terminal alkynes. We have recently shown that hydro-

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