thermodynamic studies and the estimation of ligand cone angle effects.

Summary

Thermodynamic parameters have been obtained for the binding of PMe_3, $PMe_2(C_6H_5)$, $P(OMe)_3$, $P(OEt)_3$, and PEt_3 to $Ti(2,4\text{-}C_7H_{11})_2$, as well as for PEt_3 to $Ti(3\text{-}C_6H_9)_2$. The much stronger binding of PEt_3 to $Ti(3\text{-}C_6H_9)_2$ as compared to $Ti(2,4\text{-}C_7H_{11})_2$ suggests that the binding is greatly inhibited by the presence of intramolecular CH_3–CH_3 interactions which are generated on the adoption of syn-eclipsed bis(pentadienyl)–metal configurations. These CH_3–CH_3 interactions therefore seem to be a key in allowing for the existence of the 14-electron "open titanocene", $Ti(2,4\text{-}C_7H_{11})_2$. For $Ti(2,4\text{-}C_7H_{11})_2$, the binding by phosphines may be correlated entirely with steric effects, although revisions of particularly the phosphite cone angles are required. It may be that further structural studies will aid in providing slightly better estimates of some other phosphine cone angles;[40] nevertheless, it is important to note that even with these relatively minor revisions of Tolman's early models, it is still quite clear that phosphine cone angles play an important, if not dominant, role in the binding of these ligands to metals, in accord with Tolman's conclusions. The crowded "open titanocene" adducts even provide an example of complexes in which the steric factor seems overwhelming.

Acknowledgment. R.D.E. expresses his appreciation for generous support of this research from the National Science Foundation and from the donors of the Petroleum Research Fund, administered by the American Chemical Society. We are grateful to Dr. Chad Tolman and Prof. John Verkade for very helpful discussions. The NMR and mass spectrometers were obtained through NSF and DOE instrumentation grants and with the support of the University of Utah Institutional Funds Committee.

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Mixed-Valent Cations of Dinuclear Chromium Aryl Complexes: Electrochemical, Spectroscopic, and Structural Considerations[⊥]

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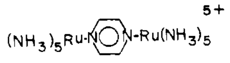
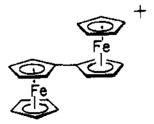
Contribution from the Departments of Chemistry, University of Vermont, Burlington, Vermont 05405, U.S. Naval Academy, Annapolis, Maryland 21402, and University of Delaware, Newark, Delaware 19716. *Received December 19, 1986*

Abstract: The oxidation of a series of six dinuclear chromium carbonyl complexes linked by a biphenyl ligand and/or a diphosphino- (or arsino-) methane moiety has been studied by electrochemistry, infrared spectroscopy, electron spin resonance spectroscopy, and X-ray crystallography. Comparison is made with four mononuclear analogues. Each dinuclear complex shows two successive one-electron oxidations, with the separation of $E°$ values varying from a low of 160 mV for $[(\text{benzene})Cr(CO)_2]_2(\mu\text{-dppm})$ (**11**, dppm = (diphenylphosphino)methane) to a high of 550 mV for $(\text{biphenyl})[Cr(CO)_2]_2(\mu\text{-dmpm})$ (**10**, dmpm = (dimethylphosphino)methane). The monocation derived from $(\text{biphenyl})[Cr(CO)_2(PPh_3)]_2$ (7^+) displays IR and ESR spectra indicative of a charge- and spin-localized mixed-valent complex. Complexes $\mathbf{8}^+$–$\mathbf{10}^+$ with both a biphenyl and diphosphino- or arsinomethane linkage are valence-delocalized, judging from IR and ESR spectra. Neutral $(\text{biphenyl})[Cr(CO)_2]_2(\mu\text{-dppm})$ (**8**) has a severe twisting of the phenyl rings, the torsion angle being 50.8°. However, the torsion angle relaxes to 3.7° in the monocation $\mathbf{8}^+$. Neutral **8** crystallizes in the space group $P\bar{1}$ with $a = 9.606$ (3) Å, $b = 13.530$ (3) Å, $c = 18.774$ (8) Å, $\alpha = 76.57$ (3)°, $\beta = 78.88$ (3)°, $\gamma = 70.04$ (3)°, and $Z = 2$. Cationic $\mathbf{8}^+[PF_6]^-$ crystallizes in the space group $C2/c$ with $a = 34.353$ (9) Å, $b = 11.185$ (2) Å, $c = 31.011$ (9) Å, $\beta = 126.18$ (2)°, and $Z = 8$.

Shortly after the appearance of the first modern theoretical treatments of mixed valency,[1,2] two important classes of mixed-valent compounds were reported. One of these originated with the pyrazine-bridged bis(pentammineruthenium) complex, A, $[(H_3N)_5Ru]_2(\mu\text{-}C_6H_4N_2)^{5+}$, containing formal Ru(II) and Ru(III).[3] The other was based on the biferrocenium ion, B, containing formal Fe(II) and Fe(III).[4] For nearly two decades parallel investigations have proceeded on both classes of compounds and their analogues to probe the factors influencing charge delocalization in dinuclear complexes. These efforts have been sustained by ancillary interest in excited-state charge transfer, low-dimensional conductivity, and other chemical and physical properties of mixed-valent compounds and lattices.[5a] Recently, enhancement of reactivity through cooperative metal effects has also received attention for these types of molecules.[5b,c] Partly because of the synthetic flexibility in designing bridging ligands



A



B

[⊥] Structural Consequences of Electron-Transfer Reactions, Part 15. For Part 14 see ref 49.

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[§] University of Delaware.

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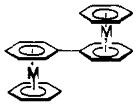
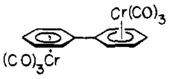
between ruthenium centers, there exists an impressive degree of understanding of delocalization through heterocyclic bridging ligands,[6] although some fundamental questions remain.[7] The success of these studies relies greatly on the substitution inertness of the two metal oxidation states involved, Ru(II) and Ru(III), which allows for reversible redox chemistry and easy spectral access to both the oxidized and reduced complexes.

Information on organometallic analogues, while still extensive and impressive, has been more limited by this requirement for substitution inertness. Organometallic investigations have been mainly limited to ferrocene as a redox site, often with imaginative efforts of linking together these units through different organic or organometallic functionalities.[8,9] Recent articles reveal that questions remain on key points such as the electronic mechanisms for delocalization[10] (whether indirect, through the bridging ligand, or direct, through a metal–metal interaction) and the role of counterion lattice mobility in charge delocalization.[11]

Our understanding of organometallic mixed-valent compounds may be extended by preparing such species from diaryl ligands, in which the larger metal–metal distance precludes a direct spatial M–M interaction.[12] To this end, valuable work on complexes like C (M = Cr, V) and their ionic derivatives has appeared,[13,14] along with studies on related iron complexes.[15,16] However, D is one of the potentially most attractive diaryl dinuclear complexes for these investigations. (Arene)chromium tricarbonyl complexes are easy to prepare from a wide array of arenes,[17] providing access to linkages with different electronic and structural requirements. Furthermore, the presence of replacable carbonyl groups on the metal opens synthetic possibilities.



C

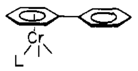


D

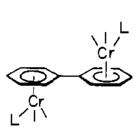
Earlier attempts at preparing cations from complexes like D or its mononuclear analogues had limited success due to instability of the Cr(I) complexes produced on one-electron oxidation of the (arene)chromium tricarbonyl moiety.[18-20] However, the phosphine-substituted analogues (arene)$Cr(CO)_2(PR_3)$ give stable oxidation products.[21] Thus, we have begun an investigation of binuclear complexes based on the (arene)$Cr(CO)_2(PR_3)$ functionality, and this paper reports the first results. The mixed-valent effects in these systems can be probed by electrochemistry, electron spin resonance (ESR) spectroscopy (through the ^{31}P "spin label"), and infrared (IR) spectroscopy (through the shift of the CO-stretching frequency, which constitutes a "charge label"). Data on compounds **1–11** are reported.

1

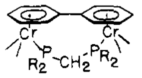
— = CO



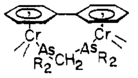
3, L = CO
4, L = PPh_3
5, L = $AsPh_3$



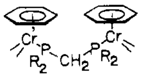
6, L = CO
7, L = PPh_3



8, R = Ph
10, R = Me



9, R = Ph



11, R = Ph

Experimental Section

Materials. Preparation of the chromium complexes has been reported.[5b] Sulfur dioxide (99.9%) was purchased from Matheson Gas Products and dried by passage through P_2O_5. All other electrochemical solvents were purchased from Burdick and Jackson, Inc., and dried by distillation from CaH_2 or $CaCl_2(CH_3NO_2)$ or, in the case of propylene carbonate, by treatment with molecular sieves. Tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) was prepared by methathesis of Bu_4NI and NH_4PF_6, recrystallized from 95% ethanol, and vacuum dried. Ferrocenium hexafluorophosphate was prepared by oxidation of Cp_2Fe with equimolar $AgPF_6$ (Ozark-Mahoning).

Electrochemical Procedures. The basic electrochemical techniques used for drybox or nitrogen blanket experiments have been described.[22] Cyclic voltammetry data using scan rates in excess of 500 mV/s were recorded on a Bascom-Turner Model 4120 digital recorder. Low-temperature electrochemical experiments in the drybox employed a FTS Systems Flexi-Cool refrigeration system which controlled the temperature to ±1 K. Electrochemistry under vacuum was performed with a cell similar to that described by Tinker and Bard,[23] and electrochemical studies in liquid SO_2 (at 243 K) followed their recommendations. The potential of a silver wire or Ag/AgCl electrode was used as a reference

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for vacuum cell work and later related to the saturated calomel electrode (SCE) potential by use of an internal standard, usually ferrocene. Liquid SO_2 gave a usable background window of ca. +3 to −0.7 V vs. Ag, and the system was checked out with the $(bpy)_3Fe^{2+/3+}$ couple, which gave the literature[23] results. Bu_4NPF_6 (0.1 M) was the supporting electrolyte in all electrochemical experiments. Platinum electrodes were employed both as small working electrodes for voltammetry and as cylindrical gauzes for coulometry. All potentials reported in this paper are referenced to the aqueous SCE.

Spectroscopic Procedures. ESR studies were performed by using a modified Varian E-4 spectrometer, and the infrared spectrometer was a Nicolet Series 600 FTIR. The short lifetime of many of the cation radicals required the design of a low-temperature flow system to obtain reliable IR spectra. Typically, about 20 mg of the neutral chromium complex was placed in a reaction vessel cooled by a low-temperature circulator (Neslab, ±1 K). Dried solvent (20 mL) (CH_2Cl_2 or CH_3NO_2) was added by cannula under dinitrogen. A solution of Cp_2Fe^+ in the same solvent was added by syringe, the ferrocenium oxidant being sufficient to produce 1 molar equiv of the chromium cation. After being stirred ca. 5 min, the solution of the oxidized complex was drawn by syringe through the IR cell, which was maintained at ca. 265 K by cold N_2 gas blowing through the IR sampling chamber. Spectra were taken over the carbonyl frequency range and were accumulated over ca. 15 s (10 scans) at a resolution of 1 cm^{-1}. Solvent and background absorptions were minimized by a subtractive ratioing program.

X-ray Structural Determinations. Crystals of **8** were grown under N_2 by allowing pentane vapor to diffuse into a concentrated benzene solution of the compound over 2 days at 298 K. The monocation **8**$^+$ was prepared by first oxidizing 60 mg of **8** with Cp_2Fe^+ in CH_2Cl_2, then concentrating the solution, and adding pentane to precipitate the cation and remove ferrocene. The resulting green solid was dried and redissolved in 2 mL of CH_3NO_2, to which diethyl ether was vapor-diffused for 2 days at 278 K. Dark green crystals of **8**$^+[PF_6]^-$ were obtained. Both crystals were mounted on glass fibers with epoxy cement. Unit-cell parameters were derived from the least-squares fit of the angular settings of 25 reflections ($20° \le 2\theta \le 30°$) chosen to include Friedel-related sets to check diffractometer and optical alignment. In both cases the choice of the centrosymmetric space group alternative ($P\bar{1}$ for **8** and $C2/c$ for **8**$^+$) was based on the computationally stable and chemically reasonable results obtained.

Data were collected at ambient temperatures (22–24 °C) on a Nicolet R3m/μ diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The intensity data were corrected for linear decay, but no correction for absorption was required (low μ's and small T_{max}/T_{min} ratios).

Both structures were solved by direct methods and completed by a series of difference Fourier syntheses.

For **8**: all non-hydrogen atoms were refined anisotropically, the hydrogen atoms were idealized (d(C–H) = 0.96 Å) as updated isotropic contributions, and the dppm phenyl rings were constrained to rigid-hexagonal geometries, d(C–C) = 1.395 Å. Two partially rotationally disordered molecules of benzene were located for each Cr_2 complex and anisotropically refined as the atoms B(1) to B(12).

For **8**$^+$: the same procedures were used as used for **8**, except that two superimposed coordination octrahedra were found for the PF_6^- counterion in the refined occupancies of 0.61 (1) for the unprimed F atoms and 0.39 (1) for the primed F atoms. The two octahedra were constrained to octahedral symmetry, and the P–F and P–F′ distances were refined as individual variables giving P–F = 1.561 (2) Å and P–F′ = 1.537 (3) Å. A difference map near convergence showed a cluster of four peaks in the 1.5–2.0 e $Å^{-3}$ range well separated from either ion and spaced at chemically reasonable distances, 1.38–1.58 Å. These peaks were incorporated as isotropic half-occupancy carbon atoms, C(w) to C(z); the R factor was lowered from 7.4 to 6.9%, but no modeling apparent to us yielded an unambiguous identification. Although presumed to be a disordered, substoichiometric molecule of solvent, its presence was not taken into account in the calculated density.

All computer programs are part of the SHELXTL (5.1) library (Nicolet Corp., Madison, WI).

Atomic coordinates are given in Tables II and III for **8** and **8**$^+$, respectively, and Table IV provides selected bond distances and angles. Additional crystallographic data are available (see supplementary material).

Results

I. Mononuclear Complexes. The electrode behavior of mononuclear chromium arene complexes provides a useful comparison with the dinuclear compounds studied in this work. Therefore, we report briefly on the oxidation of these compounds under our conditions.

Table I. Crystal Parameters, Data Collection, and Refinement for **8** and **8**$^+$

	8 (I)	**8**$^+$ (II)
compd	$[(C_6H_5)_2Cr_2(CO)_4(dppm)]\cdot 2C_6H_6$	$[(C_6H_5)_2Cr_2(CO)_4(dppm)][PF_6]$
formula	$C_{53}H_{44}Cr_2O_4P_2$	$C_{41}H_{32}Cr_2F_6O_4P_3$
cryst system	triclinic	monoclinic
space group	$P\bar{1}$	$C2/c$
a, Å	9.606 (3)	34.353 (9)
b, Å	13.530 (3)	11.185 (2)
c, Å	18.774 (8)	31.011 (9)
α, deg	76.57 (3)	
β, deg	78.88 (3)	126.18 (2)
γ, deg	70.04 (3)	
V, $Å^3$	2213.5 (16)	9618.5 (49)
Z	2	8
D(calcd), g cm^{-3}	1.37	1.24
μ(Mo Kα), cm^{-1}	6.2	6.3
cryst size, mm	0.166 × 0.16 × 0.32	0.22 × 0.24 × 0.31
cryst color	orange	green
scan technique	$\theta/2\theta$	ω
scan limits, deg	4–45	4–45
scan speed, deg min^{-1}	var 5–20	var 6–20
rflns collected	5703	6822
independent rflns	5507	6289
independent rflns with $F_o \ge n\sigma(F_o)$	3500 (n = 3)	3776 (n = 4)
R(int), %	2.3	1.6
std rflns	3 std/97 rflns	3 std/197 flns
decay, %	≤1.5	≤5.5
T_{max}/T_{min}	1.16	1.21
R_F, %	5.72	6.94
R_{wF}, %	6.02	7.09
GOF	1.19	1.46
Δ/σ(max)	0.06	0.09
$\Delta\rho$(max), e $Å^{-3}$	0.37	1.01
N_0/N_v	7.0	7.1

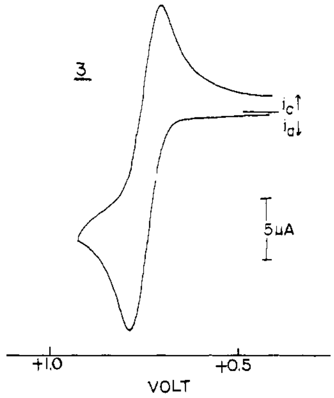

Figure 1. CV scan of (biphenyl)$Cr(CO)_3$ (**3**) (4×10^{-4} M in CH_2Cl_2 at a Pt electrode, T = 263 K, v = 0.20 V s^{-1}).

As noted by several groups[19,20,24] and investigated in depth by Rieke and co-workers,[18,25] cation radicals of (arene)chromium tricarbonyl complexes require solvents of unusually low nucleophilicity for stability. Consistent with these findings, (biphenyl)$Cr(CO)_3$ (**3**) oxidizes irreversibly at 298 K in CH_2Cl_2/0.1 M Bu_4NFP_6 but oxidizes reversibly in this medium at reduced temperatures. Although a temperature of 233 K was necessary to suppress completely the decomposition of (**3**)$^+$, voltammograms at 263 K showed sufficient return current to allow calculation of the $E°$ of this system (Figure 1, Table V).[26] Comparison of CV

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(24) (a) Lloyd, M. K.; McCleverty, J. A.; Connor, J. A.; Jones, E. M. *J. Chem. Soc., Dalton Trans.* **1973**, 1768. (b) Gubin, S. P.; Khandkarova, V. S. *J. Organomet. Chem.* **1970**, *22*, 449. (c) Degrand, C.; Radecki-Sudre, A.; Besancon, J. *Organometallics* **1982**, *1*, 1311. (d) Ikeshoji, T.; Parker, V. D. *Acta Chem. Scand., Ser. B* **1983**, *B37*, 715.

(25) (a) Rieke, R. D.; Milligan, S. N.; Tucker, I.; Dowler, K. A.; Willeford, B. R. *J. Organomet. Chem.* **1981**, *218*, C25. (b) Rieke, R. D.; Tucker, I.; Milligan, S. N.; Wright, D. R.; Willeford, B. R.; Radonovich, L. J.; Eyring, M. W. *Organometallics* **1982**, *1*, 938.

Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for **8**

	x	*y*	*z*	*U*^{a}
Cr(1)	5237 (1)	3618 (1)	2639 (1)	29 (1)
Cr(2)	2854 (1)	6935 (1)	1092 (1)	34 (1)
P(1)	6774 (2)	4663 (1)	2442 (1)	28 (1)
P(2)	4404 (2)	7031 (1)	1879 (1)	31 (1)
O(1)	3022 (5)	4771 (4)	3754 (3)	53 (2)
O(2)	6752 (6)	2207 (4)	3927 (3)	61 (2)
O(3)	5502 (6)	6794 (5)	-52 (3)	68 (3)
O(4)	1859 (6)	9316 (4)	650 (3)	70 (3)
C(1)	3910 (7)	4361 (5)	3312 (3)	37 (3)
C(2)	6204 (7)	2757 (5)	3417 (3)	36 (3)
C(3)	4466 (8)	6883 (6)	392 (4)	44 (3)
C(4)	2280 (8)	8393 (6)	840 (4)	45 (3)
C(5)	6297 (6)	6025 (5)	1874 (3)	31 (3)
C(11)	3304 (7)	3478 (5)	2290 (3)	36 (3)
C(12)	4219 (8)	2442 (5)	2520 (4)	42 (3)
C(13)	5721 (8)	2140 (5)	2204 (4)	47 (3)
C(14)	6259 (8)	2860 (5)	1658 (4)	44 (3)
C(15)	5326 (8)	3890 (5)	1429 (3)	38 (3)
C(16)	3820 (7)	4214 (5)	1726 (3)	32 (3)
C(21)	2786 (7)	5256 (5)	1461 (3)	30 (3)
C(22)	1766 (7)	5918 (5)	1950 (4)	38 (3)
C(23)	672 (8)	6838 (6)	1697 (4)	47 (3)
C(24)	566 (7)	7154 (6)	927 (4)	55 (4)
C(25)	1541 (8)	6528 (6)	438 (4)	52 (4)
C(26)	2657 (7)	5601 (5)	697 (4)	39 (3)
C(31)	8612 (4)	5301 (4)	3112 (2)	43 (3)
C(32)	9074	5525	3700	52 (4)
C(33)	8349	5333	4413	51 (4)
C(34)	7163	4916	4538	43 (3)
C(35)	6701	4692	3949	35 (3)
C(36)	7425	4885	3236	31 (3)
C(41)	9409 (5)	3026 (3)	2290 (2)	51 (3)
C(42)	10750	2436	1939	54 (4)
C(43)	11304	2855	1233	49 (4)
C(44)	10516	3864	878	52 (4)
C(45)	9175	4454	1229	44 (3)
C(46)	8621	4035	1935	30 (3)
C(51)	6091 (5)	8281 (3)	944 (2)	45 (3)
C(52)	6413	9235	643	60 (4)
C(53)	5602	10160	929	66 (4)
C(54)	4469	10131	1516	62 (4)
C(55)	4147	9177	1817	52 (3)
C(56)	4958	8253	1531	35 (3)
C(61)	4822 (4)	7193 (4)	3287 (3)	51 (4)
C(62)	4335	7375	4008	65 (4)
C(63)	2837	7542	4293	69 (4)
C(64)	1825	7527	3856	62 (4)
C(65)	2311	7346	3135	49 (3)
C(66)	3809	7179	2850	41 (3)
B(1)	9430 (11)	5 (8)	2237 (6)	80 (5)
B(2)	9307 (13)	42 (8)	2956 (7)	103 (7)
B(3)	8345 (14)	-348 (9)	3478 (6)	116 (7)
B(4)	7517 (13)	-873 (9)	3253 (9)	109 (7)
B(5)	7708 (10)	-917 (7)	2514 (6)	92 (5)
B(6)	8640 (12)	-489 (8)	2027 (6)	84 (6)
B(7)	697 (12)	1457 (11)	4252 (6)	107 (7)
B(8)	1003 (18)	2324 (10)	4335 (6)	125 (8)
B(9)	2429 (21)	2205 (11)	4440 (6)	118 (9)
B(10)	3477 (12)	1231 (9)	4455 (5)	114 (7)
B(11)	3105 (13)	407 (8)	4358 (6)	108 (6)
B(12)	1747 (14)	539 (9)	4256 (6)	112 (7)

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

peak separations and anodic current heights with those of ferrocene established the process as a diffusion-controlled one-electron wave.[27]

Table III. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for $\mathbf{8}^+$

	x	*y*	*z*	*U*
Cr(2)	3533 (1)	5611 (1)	-188 (1)	51 (1)^a
Cr(1)	4367 (1)	2413 (1)	38 (1)	51 (1)^a
P(1)	3577 (1)	2090 (2)	-753 (1)	43 (1)^a
P(2)	2989 (1)	4535 (2)	-986 (1)	45 (1)^a
P(3)	1014 (1)	-144 (3)	2054 (1)	85 (2)^a
F(1)	455 (2)	-26 (11)	1704 (3)	154 (10)^a
F(2)	975 (4)	-1477 (5)	1917 (3)	198 (21)^a
F(3)	1017 (4)	213 (8)	1573 (4)	177 (19)^a
F(4)	1055 (4)	1221 (5)	2210 (4)	159 (15)^a
F(5)	1018 (4)	-462 (7)	2551 (3)	118 (11)^a
F(6)	1579 (2)	-222 (8)	2420 (4)	166 (10)^a
F(1′)	997 (4)	-696 (11)	1582 (3)	156 (16)^a
F(2′)	1411 (4)	-1059 (9)	2429 (4)	260 (32)^a
F(3′)	1409 (3)	713 (9)	2150 (5)	114 (14)^a
F(4′)	627 (3)	755 (9)	1661 (4)	177 (22)^a
F(5′)	628 (4)	-1051 (10)	1943 (5)	173 (29)^a
F(6′)	1050 (5)	395 (12)	2529 (4)	257 (27)^a
C(26)	4313 (3)	5928 (8)	435 (4)	62 (6)^a
C(25)	4061 (3)	6983 (8)	389 (4)	70 (6)^a
C(24)	3762 (4)	7525 (7)	-110 (4)	73 (7)^a
C(23)	3696 (3)	7063 (7)	-563 (4)	68 (6)^a
C(22)	3952 (3)	5988 (8)	-516 (4)	59 (6)^a
C(21)	4280 (3)	5427 (7)	-13 (4)	51 (5)^a
C(16)	4545 (3)	4362 (8)	44 (4)	54 (6)^a
C(11)	4484 (3)	3783 (8)	-407 (4)	64 (6)^a
C(12)	4761 (4)	2734 (10)	-329 (5)	81 (8)^a
C(13)	5083 (4)	2255 (10)	190 (6)	94 (9)^a
C(14)	5154 (4)	2792 (9)	632 (5)	83 (7)^a
C(15)	4889 (3)	3811 (9)	556 (4)	71 (6)^a
C(4)	2990 (3)	6235 (7)	-273 (4)	62 (6)^a
C(3)	3535 (3)	4644 (9)	294 (4)	69 (6)^a
C(1)	4255 (4)	2380 (8)	547 (4)	73 (6)^a
C(2)	4404 (3)	769 (10)	120 (4)	68 (6)^a
C(5)	3217 (3)	3359 (6)	-1200 (3)	41 (4)^a
O(4)	2658 (3)	6609 (6)	-303 (3)	96 (5)^a
O(3)	3519 (3)	4156 (8)	618 (3)	108 (6)^a
O(1)	4219 (3)	2288 (8)	898 (3)	119 (7)^a
O(2)	4445 (3)	-260 (6)	194 (3)	89 (5)^a
C(61)	2396 (2)	6457 (5)	-1586 (3)	66 (6)^a
C(62)	2241	7425	-1935	92 (8)^a
C(63)	2414	7575	-2241	93 (8)^a
C(64)	2742	6757	-2197	76 (7)^a
C(65)	2897	5789	-1848	61 (6)^a
C(66)	2724	5639	-1543	57 (5)^a
C(51)	2410 (2)	3549 (5)	-707 (2)	58 (6)
C(52)	1995	3010	-814	71 (7)
C(53)	1606	2772	-1340	77 (7)
C(54)	1632	3073	-1759	74 (6)
C(55)	2047	3612	-1652	68 (6)
C(56)	2436	3850	-1126	48 (5)
C(41)	3239 (2)	809 (5)	-251 (2)	56 (6)
C(42)	2906	118	-242	72 (7)
C(43)	2462	-163	-718	77 (8)
C(44)	2352	247	-1204	73 (7)
C(45)	2685	939	-1213	60 (6)
C(46)	3128	1220	-736	45 (5)
C(31)	3814 (3)	1005 (6)	-1852 (2)	94 (9)
C(32)	3802	-238	-1827	87 (8)
C(33)	3708	-775	-1491	75 (7)
C(34)	3627	-69	-1180	62 (6)
C(35)	3640	1175	-1206	43 (5)
C(36)	3733	1712	-1542	70 (7)
Cx	4239 (9)	8318 (23)	1461 (10)	111 (8)
Cy	3738 (14)	8656 (35)	1347 (15)	186 (14)
Cz	4136 (20)	6930 (47)	1640 (21)	250 (22)
Cw	3688 (18)	7460 (42)	1414 (17)	209 (17)

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

Comparative studies in propylene carbonate were surprising because the oxidation was *less* reversible in this solvent, showing no return cathodic current at 263 K. Propylene carbonate with tetraethylammonium perchlorate as supporting electrolyte had been shown to be reasonably unreactive toward (arene)chromium tricarbonyl cations.[25] The enhanced stability we observe for these species in dichloromethane over propylene carbonate may arise from ion-pairing of the cation with PF_6 anion, which should be stronger in the less polar CH_2Cl_2.[28]

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(26) A second oxidation wave of **3** occurred at E_p = +1.38 V. It was irreversible by cyclic voltammetry and was not studied further.

(27) Details of these measurements are available: VanOrder, N., Jr., Ph.D. Dissertation, University of Vermont, 1986.

Table IV. Selected Bond Distances and Angles for **8** and **8**$^+$

	8 (neutral)	**8**$^+$ (cation)
(a) Bond Distances (Å)		
Cr(1)–CNT(1)	1.699 (7)	1.731 (9)
Cr(2)–CNT(2)	1.696 (7)	1.747 (9)
	av 1.698 (3)[a]	av 1.739 (a)
Cr(1)–P(1)	2.229 (2)	2.378 (2)
Cr(2)–P(2)	2.343 (2)	2.367 (2)
	av 2.321	av 2.373 (7)
Cr(1)–C(1)	1.823 (6)	1.83 (1)
Cr(1)–C(2)	1.831 (6)	1.85 (1)
Cr(2)–C(3)	1.820 (7)	1.84 (1)
Cr(2)–C(4)	1.829 (8)	1.86 (1)
	av 1.826 (5)	av 1.85 (1)
Cr(1)···Cr(2)	4.828 (1)	4.374 (2)
C(16)–C(2)	1.459 (8)	1.45 (1)
(b) Bond Angles (deg)		
CNT(1)–Cr(1)–P(1)	125.2 (2)	127.9 (3)
CNT(2)–Cr(2)–P(2)	132.5 (2)	125.1 (3)
CNT(1)–Cr(1)–C(1)	125.2 (3)	121.4 (4)
CNT(1)–Cr(1)–C(2)	124.7 (3)	124.1 (4)
CNT(2)–Cr(2)–C(3)	125.7 (3)	126.5 (4)
CNT(2)–Cr(2)–C(4)	123.0 (3)	123.7 (4)
P(1)–Cr(1)–C(1)	93.5 (3)	101.0 (3)
P(1)–Cr(1)–C(2)	90.3 (3)	86.3 (2)
P(2)–Cr(2)–C(3)	84.8 (3)	99.9 (3)
P(2)–Cr(2)–C(4)	88.9 (3)	86.4 (3)
C(1)–Cr(1)–C(2)	86.9 (3)	83.9 (5)
C(3)–Cr(2)–C(4)	88.5 (3)	81.8 (5)
Cr(1)–P(1)–C(5)	121.8 (2)	120.4 (2)
Cr(2)–P(2)–C(5)	116.6 (2)	119.9 (2)
P(1)–C(5)–P(2)	125.7 (3)	120.9 (5)
(c) Dihedral Angle (deg)		
biphenyl twist	50.8 (3)	3.7 (4)

[a] Esd's from $(n - 1)$ scatter formula.

Table V. Standard Potentials vs. SCE of Chromium Arene Complexes in CH_2Cl_2/0.1 M Bu_4NPF_6[a,b]

complex		$E_1°$, mV	$E_2°$, mV	$E_2 - E_1°$, mV
(benzene)Cr(CO)$_3$	**1**	800	...	ref 18
(biphenyl)Cr(CO)$_3$	**3**	800 (263 K)	...	...
(biphenyl)Cr(CO)$_2$(PPh$_3$)	**4**	320	...	...
(biphenyl)Cr(CO)$_2$(AsPh$_3$)	**5**	340	...	...
(biphenyl)[Cr(CO)$_3$]$_2$	**6**	800 (260 K)	≥1000	200
(biphenyl)[Cr(CO)$_2$(PPh$_3$)]$_2$	**7**	260 (273 K)	520	260
(biphenyl)[Cr(CO)$_2$]$_2$(μ-dppm)	**8**	100	640	540
(biphenyl)[Cr(CO)$_2$]$_2$(μ-dpam)	**9**	170	670	500
(biphenyl)[Cr(CO)$_2$]$_2$(μ-dmpm)	**10**	40	590	550
[(benzene)Cr(CO)$_2$]$_2$(μ-dppm)	**11**	510 (273 K)	670	160

[a] Unless otherwise noted, temperature was 298 K. [b] $E°$ potential calculated from the average of the anodic and cathodic CV peak potentials.

The phosphine- and arsine-substituted derivatives (biphenyl)Cr(CO)$_2$(EPh$_3$) [**4**, E = P; **5**, E = As] gave far more stable cations, ones which could be characterized by spectroscopic methods. CV studies of **4** in CH_2Cl_2 at 298 K showed a diffusion-controlled wave at $E° = +0.32$ V which was highly reversible both chemically and electrochemically. For example, a CV peak separation of 62 mV was measured when the scan rate was 0.02 V s^{-1}. The reversibility of $\mathbf{4} \rightleftarrows \mathbf{4}^+$ was confirmed by double potential-step chronoamperometry,[29] and a diffusion coefficient of 2.03×10^{-5} cm^2 s^{-1} was calculated for **4**.[30] **4**$^+$ did not display indefinite stability. Solutions of the cation could be produced either by bulk coulometry or by oxidation using an equimolar amount of [Cp$_2$Fe][PF$_6$]. Monitoring of these solutions by RPE voltammetry demonstrated disappearance of the waves for the **4**/**4**$^+$ couple within 10 min at 298 K. The cation was even less stable in propylene carbonate.

Almost identical behavior was observed for the oxidation of the AsPh$_3$ derivative **5** for which $E° = +0.34$ V. Under very stringent conditions (vacuum electrolysis cell/CH_2Cl_2/273 K) the half-life of **5**$^+$ was ca. 15 min. The color of the cations did not appear to be greatly different from that of their neutral precursors, since solutions of **4**$^+$ and **5**$^+$ simply showed a darkening of the original yellow of the neutrals.

The reasonable longevity of **4**$^+$ allowed both ESR and IR spectra of this cation to be recorded. For ESR studies, a 1:1 mixture of dichloromethane and 1,2-dichloroethane was used as solvent and the oxidation performed under vacuum at 273 K using Cp$_2$Fe$^+$ (ca. 1 mM in oxidant and **4**). Freezing the reaction solution produced a spectrum with a rhombic **g** tensor and a doublet due to ^{31}P hyperfine splitting (hfs) around each **g** tensor feature. The phosphorus hfs was nearly isotropic, with an average value of 20.6 G (Table VI). Attempts at measuring fluid solution spectra of **4**$^+$ failed, apparently due to instability of the cation since melting (at 193 K) and refreezing the solution resulted in loss of the signal.

IR spectra of **4**$^+$ were obtained with the flow system described in the Experimental Section. Millimolar solutions of **4** and Cp$_2$Fe$^+$ in CH_2Cl_2 were mixed at 203 K and pumped into the IR sample chamber, which was kept at ca. 265 K. The spectrum recorded 15 s after **4**$^+$ had entered the sample chamber contained two bands in the CO-stretching region (1933, 1886 cm^{-1}). During the next 60 s this pair of absorptions was replaced by another pair at ν_{CO} = 1887 and 1833 cm^{-1} (Table VII) belonging to the neutral precursor **4**. Thus, these measurements confirm earlier observations[21] that the asymmetric CO stretch of [(arene)Cr(CO)$_2$(PR$_3$)]$^+$ falls at a frequency which is indistinguishable from that of the symmetric CO stretch of [(arene)Cr(CO)$_2$(PR$_3$)]. This fact will be important (vide infra) in interpretation of the IR spectrum of (biphenyl)[Cr(CO)$_2$(PPh$_3$)]$_2$$^+$.

These experiments on the electrochemical and spectroscopic characterization of the mononuclear Cr(I) complexes are consistent with the findings of Connelly et al., who obtained spectroscopic data on more stable analogues containing methylated arene rings,[21] and establish that even relatively unstable cations can be reliably characterized by our methods. More importantly, they give us ESR and IR parameters for "fully oxidized" Cr(I) complexes to aid comparison with dinuclear complexes which may display charge delocalization.

II. Dinuclear Complexes. 1. (Biphenyl)[Cr(CO)$_2$L]$_2$ [L = CO (6) or PPh$_3$ (7)]. The electrochemical oxidation of (biphenyl)[Cr(CO)$_3$]$_2$ (**6**) was shown earlier[25b] to occur in a single irreversible two-electron wave. At ambient temperatures we also observe this behavior. As the temperature was lowered, this wave decreased its height to that appropriate for a one-electron process, and the wave became increasingly chemically reversible. At the same time, a second one-electron wave was observed at more positive potentials (Figure 2). This observation allows us to calculate approximate $E°$ values for the successive one-electron processes:

$$\mathbf{6} \rightleftarrows \mathbf{6}^+ + e^- \quad E° = +0.80 \text{ V}$$

$$\mathbf{6}^+ \rightleftarrows \mathbf{6}^{2+} + e^- \quad E° = \text{ca. } +1.00 \text{ V}$$

At 260 K, the first oxidation fulfilled CV criteria for a diffusion-controlled reversible one-electron process,[27,31] establishing that the monocation **6**$^+$ was persistent for short times. Oxidation of **6**$^+$ to **6**$^{2+}$ was not reversible even at 233 K using v = 100 V s^{-1}, meaning that the dication is very unstable. However, an approximate $E°$ value of 1.00 V can be assigned to this reaction[32]

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[28] Ion pairing by PF$_6^-$ has been postulated as being responsible for the enhanced stability of a number of organometallic cations, including that derived from (benzene)chromium tricarbonyl: Stone, N.; Sweigart, D.; Bond, A. M. *Organometallics* **1986**, *5*, 2553.

[29] Schwarz, W. M.; Shain, I. *J. Phys. Chem.* **1965**, *69*, 30.

[30] Adams, R. N. *Electrochemistry at Solid Electrodes*; Marcel Dekker: New York, 1969; pp 214–219.

[31] For example, ΔE_p values were 65 ± 5 mV over the scan rate range of 30 mV s^{-1} to 500 mV s^{-1} (within experimental error of those of Cp$_2$Fe$^{+/0}$ or Cp$_2$Co$^{+/0}$), the width of the CV wave ($E_p - E_{p/2}$) was 60 mV, and the anodic current function was constant vs. scan rate and within 20% of that of Cp$_2$Fe$^{+/0}$.

Table VI. ESR Data for Cation Radicals of Chromium Arene Complexes in CH_2Cl_2 (Fluid) or $CH_2Cl_2/C_2H_4Cl_2$ (Frozen)

	fluid soln		frozen soln	
	$\langle g \rangle$	$\langle a_p \rangle$, G	g	A(P), G
$(\eta^6\text{-}C_6Me_6)Cr(CO)_2(PPh_3)^+$ (ref 21)			2.102	29.7 (1)[a]
			2.026	33.6 (1)
			1.992	30.5 (1)
$(biphenyl)Cr(CO)_2(PPh_3)^+$ (**4**$^+$)			2.103	29.9 (1)[a]
			2.034	32.4 (1)
			1.992	29.4 (1)
$(biphenyl)[Cr(CO)_2(PPh_3)]_2^+$ (**7**$^+$)			2.098	27.9 (1)[a]
			2.033	31.6 (1)
			1.991	30.4 (1)
$(biphenyl)[Cr(CO)_2]_2(\mu\text{-dppm})^+$ (**8**$^+$)	2.017	12.8 (2)[a]	unresolved	
$(biphenyl)[Cr(CO)_2]_2(\mu\text{-dpam})^+$ (**9**$^+$)	2.019	13.7 (2)[b]	unresolved	
$(biphenyl)[Cr(CO)_2]_2(\mu\text{-dmpm})^+$ (**10**$^+$)	2.022	14.9 (2)[a]	2.059	14.7 (2)[a]
			2.008	14.0 (2)
			1.997	14.8 (2)

[a] Number of equivalent ^{31}P nuclei with this hyperfine interaction. [b] Arsenic hyperfine splitting, two equivalent nuclei.

Table VII. Carbonyl Stretching Frequencies of Chromium Arene Complexes in CH_2Cl_2

	complex	charge	obsd absorptions (cm^{-1})
	$(\eta^6\text{-}C_6Me_6)Cr(CO)_2(PPh_3)$	0	1857, 1796
		+	1969, 1853 (ref 21)
4	$(biphenyl)Cr(CO)_2(PPh_3)$	0	1887, 1833
		+	1993, 1886
7	$(biphenyl)[Cr(CO)_2(PPh_3)]_2$	0	1888, 1834
		+	1994, 1887, 1834
8	$(biphenyl)[Cr(CO)_2]_2(\mu\text{-dppm})$	0	1886, 1835
		+	1965, 1905
9	$(biphenyl)[Cr(CO)_2]_2(\mu\text{-dpam})$	0	1887, 1836
		+	1966, 1904
10	$(biphenyl)[Cr(CO)_2]_2(\mu\text{-dmpm})$	0	1871, 1822
		+	1964, 1894

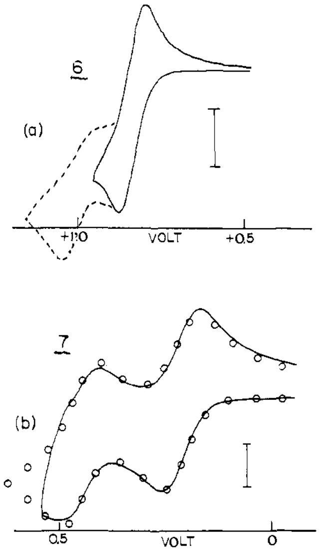

Figure 2. (a) CV scans of $(biphenyl)[Cr(CO)_3]_2$ (**6**) (4×10^{-4} M in CH_2Cl_2 at Pt, T = 260 K, v = 0.40 V s^{-1}): solid line, scan through first wave only; dotted line, second wave included. (b) CV scan (solid line) of $(biphenyl)[Cr(CO)_2(PPh_3)]_2$ (**7**) 3×10^{-4} M in CH_2Cl_2 at Pt (T = 273 K, v = 0.20 V s^{-1}). Circles give calculated curves for reversible EE mechanism using $E_1°$ = +0.26 V and $E_2°$ = 0.52 V.

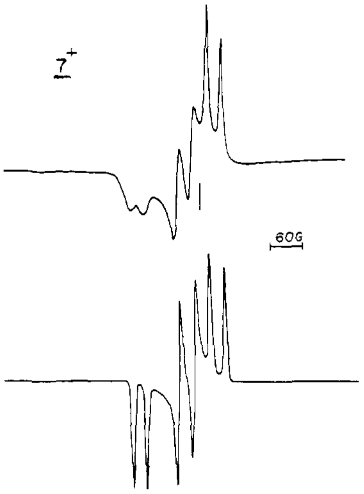

Figure 3. Experimental (top) and calculated (bottom) ESR spectra of **7**$^+$ (ca. 10^{-3} M) in a $CH_2Cl_2/C_2H_4Cl_2$ glass at 77 K. Parameters for the simulation are given in Table VI. The small vertical line gives the position of the dpph resonance.

with the understanding that it is the lower limit of the true $E°$. That is, a minimum of 200-mV separation is found for the two successive oxidations of the dinuclear biphenyl compound **6**. Bulk electrolysis at 233 K in CH_2Cl_2 failed to produce solutions of **6**$^+$ suitable for spectroscopic study, due to decay of the monocation.

The phosphine-substituted analogue $(biphenyl)[Cr(CO)_2(PPh_3)]_2$ (**7**) gave rise to more stable oxidation products. At 273 K this complex had two anodic waves at $E°$ = +0.26 and +0.52 V assigned to the couples **7**/**7**$^+$ and **7**$^+$/**7**$^{2+}$, respectively. The $E°$ separation of 260 mV is consistent with results on the carbonyl analogue **6**, for which a separation of ≥200 mV was estimated in the previous paragraph. A theoretical voltammogram employing these $E°$ values is in good agreement with the measured voltammogram (Figure 2), although at 273 K the second wave required scan rates in excess of 1 V s^{-1} to attain complete chemical reversibility.

Bulk electrolysis of yellow **7** using E_{app} = +0.37 V under vacuum at 233 K produced maroon **7**$^+$ in a clean one-electron process (1.01 F passed). The monocation was also produced quantitatively by oxidation with equimolar Cp_2Fe^+ in a reaction that was followed by rotating platinum electrode (RPE) voltammetry at 268 K. Even under these conditions **7**$^+$ decomposed within 10 min to a yellow solution containing neutral **7** and unidentified products with cathodic waves at −0.7 and −1.3 V.

One millimolar **7** treated with ferrocenium ion at 273 K in a $CH_2Cl_2/C_2H_4Cl_2$ mixture gave a deep maroon solution with a strong ESR signal (Figure 3). This spectrum was readily interpreted in terms of a rhombic **g** tensor with a resolved doublet along each of the three principal directions arising from a single ^{31}P nucleus. The phosphorus hyperfine splitting shows little anisotropy (Table VI) and the average splitting is calculated to be 30.0 G. The spectral parameters are very close to those observed for the mononuclear **4**$^+$ and suggest that the unpaired spin density

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(32) This statement assumes that the heterogeneous charge-transfer rate for **6**$^{+/2+}$ is reasonably rapid, an assumption supported by the shape and width of the wave. Very rapid decomposition of **6**$^{2+}$ would allow the wave to appear at a potential negative of its $E°$ potential. Each order of magnitude decrease in lifetime of **6**$^{2+}$ below about 10^{-2} s would introduce an error of about 30 mV into the estimation of the $E°$ value.

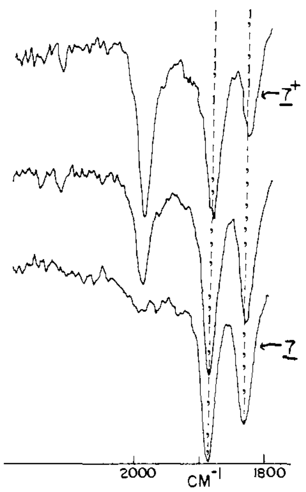

Figure 4. IR spectra of solutions containing 7^+ and/or 7 at 263 K in CH_2Cl_2. From top to bottom, the spectra were taken 15, 35, and 60 s, respectively, after introduction of a solution of 7^+ into the cell. After 60 s, the solution consisted almost entirely of neutral **7**. The dashed lines show the absorptions viewed for **7** in a separate experiment.

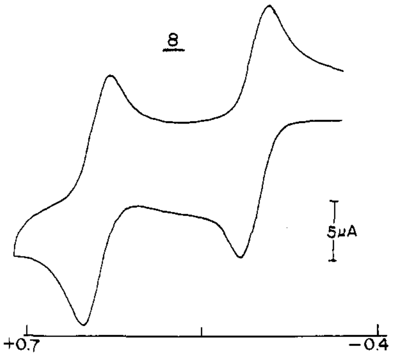

Figure 5. CV scan of (biphenyl)[Cr(CO)$_2$]$_2$(μ-dppm) (**8**) (3×10^{-4} M in CH_2Cl_2 at Pt, T = 298 K, v = 0.20 V s^{-1}).

in $\mathbf{7}^+$ is essentially localized on one side of the molecule.

Infrared studies confirm that $\mathbf{7}^+$ is a localized mixed-valent complex. If the two sides of the molecule are electronically decoupled, the IR spectrum should in principle show two sets of carbonyl doublets—one for the oxidized [Cr(I)] site and one for the unoxidized [Cr(O)] site. Since the energies of the symmetric CO stretch of the Cr(0) site and the asymmetric CO stretch of the Cr(I) site are expected to be similar (vide ante, Results, section I), three bands are predicted for the cation $\mathbf{7}^+$, as observed (Figure 4). One millimolar **7** was oxidized by Cp_2Fe^+ at 213 K in CH_2Cl_2, and IR spectra were obtained at 265 K. The bands at 1994 and 1888 cm^{-1} are assigned to the Cr(I) site, leaving 1888 and 1834 cm^{-1} as the bands assigned to the unoxidized Cr(0) site. Within about 2 min $\mathbf{7}^+$ decayed to **7**, leaving only the doublet at 1888 and 1834 cm^{-1} characteristic of the neutral complex.

2. The Doubly Bridged Complexes. (Biphenyl)[Cr(CO)$_2$]$_2$(μ-dppm) (**8**), (biphenyl)[Cr(CO)$_2$]$_2$(μ-dpam) (**9**), and (biphenyl)[Cr(CO)$_2$]$_2$(μ-dmpm) (**10**) all give two highly reversible one-electron oxidations. The monocations of this series were easily characterized by ESR and IR spectroscopy and, in the case of $\mathbf{8}^+$, by X-ray crystallography.

CV in CH_2Cl_2 showed two well-separated waves for these complexes (Figure 5) with $\Delta E°$ values of 540 (**8**), 500 (**9**), and 550 mV (**10**). With one exception, namely, the process $\mathbf{10}^+/\mathbf{10}^{2+}$, each wave was reversible in both the chemical and electrochemical sense at 298 K using scan rates below 500 mV s^{-1}. The second oxidation of **10** required temperatures below 273 K for chemical reversibility at these scan rates.

Bulk coulometry of **8** or **9** positive of the first wave released 1.0 F as the solution changed from orange to the green of the monocation. Electroyses were generally conducted at 250–270 K, the half-lives of the cations being about 1 h under these conditions. RPE scans after electrolysis (Figure 6) or after treatment of **8** with equimolar ferrocenium ion indicated quantitative formation of the monocation. It was hoped that the dications of these species would also prove isolable, but to date this has not been achieved. When $\mathbf{8}^+$ was oxidized by another electron (E_{app} = +0.82 V, 273 K), a deep blue solution of $\mathbf{8}^{2+}$ was formed (1.0 F) which decomposed within a few minutes to a mixture of **8**, $\mathbf{8}^+$, and an uncharacterized complex.

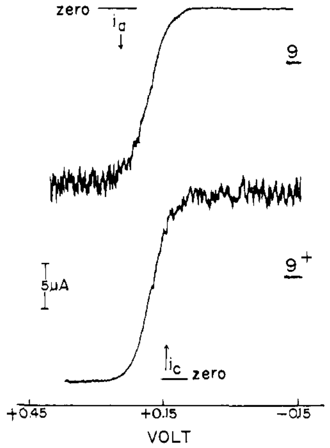

Figure 6. RPE scans of (biphenyl)[Cr(CO)$_2$]$_2$(μ-dpam) (**9**) (7×10^{-4} M in CH_2Cl_2 at 253 K) before (top) and after (bottom) electrolysis at +0.35 V. The zero current position is indicated for both scans.

Attempts to form the dications in liquid SO_2 were thwarted by their low solubility, which led to electrode passivation. When **9** was dissolved in SO_2, spontaneous formation of $\mathbf{9}^+$ occurred due to the mild oxidizing ability of SO_2.[33] CV scans through the second wave filmed the platinum electrode, with lower currents being seen after each pass through the wave. Bulk electrolysis positive of the second oxidation wave rapidly passivated the Pt gauze electrode.

ESR spectra of $\mathbf{8}^+$, $\mathbf{9}^+$, and $\mathbf{10}^+$ were observed both from electrolyzed solutions of the neutral precursors and from solutions treated with Cp_2Fe^+. Both fluid and frozen solution spectra were observed for each monocation. The phosphino derivatives $\mathbf{8}^+$ and $\mathbf{10}^+$ displayed fluid solution triplets due to interaction with two equivalent ^{31}P nuclei ($\langle a \rangle_P$ = 12.8 and 14.9 G, respectively). The arsino derivative $\mathbf{9}^+$ gave an analogous seven-line spectrum due to two equivalent As nuclei ($\langle a \rangle_{As}$ = 13.7 G). Since both P (or As) atoms of the bridging ligand are equally involved, a delocalized electronic structure is indicated. The magnitude of the P splitting is about half that observed for the mononuclear Cr(I) complex $\mathbf{4}^+$, consistent also with a valence-delocalized description of $\mathbf{8}^+$ and $\mathbf{10}^+$.

Frozen solution spectra of $\mathbf{8}^+$ and $\mathbf{9}^+$ were highly overlapped and defied reliable interpretation. This was not the case with $\mathbf{10}^+$, which gave a rhombic spectrum (Figure 7) interpreted as arising from nearly isotropic interaction with two equivalent phosphorus nuclei (Table VI). Again, the average ^{31}P hyperfine splitting in the glass (14.5 G) is about half of that observed for a mononuclear Cr(I), suggesting electronic delocalization between the two metals in the frozen as well as fluid media.

Infrared spectra of $\mathbf{8}^+$–$\mathbf{10}^+$ confirmed that the doubly bridged cations are charge-delocalized. IR spectra were easily obtained because the monocations were long-lived. Solutions of $\mathbf{8}^+$ or $\mathbf{9}^+$ were prepared either by electrochemical oxidation of the neutrals or by ferrocenium ion oxidation, with identical results. The (dimethylphosphino)methane derivative $\mathbf{10}^+$ was prepared by ferrocenium ion oxidation at 298 K. In each case the two carbonyl bands of the neutral complex were replaced by a new pair of bands (Figure 8) at an average of 75–80 cm^{-1} higher energy (Table VII). These shifts are significantly less than those observed for mono-

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(33) This property of SO_2 has received prior attention: Sharp, P. R.; Bard, A. J. *Inorg. Chem.* **1983**, *22*, 2689.

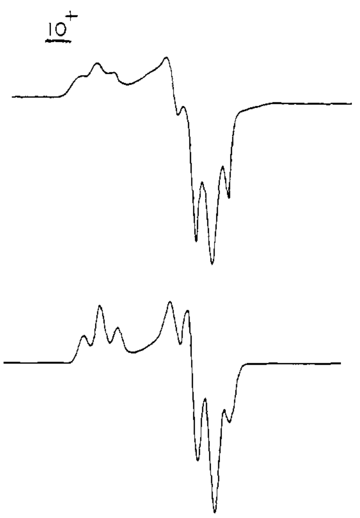

Figure 7. Experimental (top) and calculated (bottom) ESR spectra of 10^+ in a $CH_2Cl_2/C_2H_4Cl_2$ glass at 77 K. Parameters for calculation are as given in Table VI.

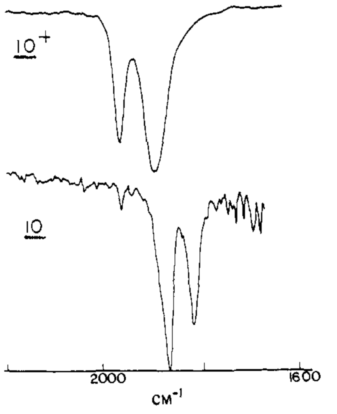

Figure 8. IR spectra of (top) 10^+ and (bottom) **10** in CH_2Cl_2 at 298 K. The cation was prepared by using Cp_2Fe^+ as oxidant.

nuclear Cr(I) complexes or the oxidized half of the localized mixed-valent cation 7^+. Since the single pair of bands implies equal charge on the two chromium atoms of 8^+–10^+, the metals are assigned a Cr(0.5) oxidation state and the doubly bridged cations are viewed as delocalized mixed-valent complexes even on the vibrational time scale.

It should be noted that unlike the *singly bridged* cationic complexes, the doubly-bridged cations 8^+–10^+ did not regenerate the original neutral complexes on standing. Rather, as the dark green solutions of the cations decomposed to yellow, there was a complete loss of IR activity in the CO region.

3. Structures of 8 and 8^+. The structures of the neutral complex **8** and the radical cation 8^+ are shown in Figures 9 and 10, respectively. Both molecules exhibit no unusually short intermolecular or interionic contacts and may, therefore, be described as containing units sufficiently well separated to prevent attributing major structural features to "packing phenomena".

Any investigation of charge or spin delocalization in biphenyl derivatives must address the question of the relative orientation of the two phenyl rings. The crystal structure of what might be viewed as the parent complex of this series, i.e., (biphenyl)[Cr(CO)$_3$]$_2$ (**6**), has been reported.[34a] Two pertinent features are the coplanar phenyl rings (torsion angle 0°) and trans Cr(CO)$_3$ units. In contrast, the 50.8 (3)° torsion angle of **8** in the biphenyl ring system is most striking. When the CrL$_3$ units are constrained

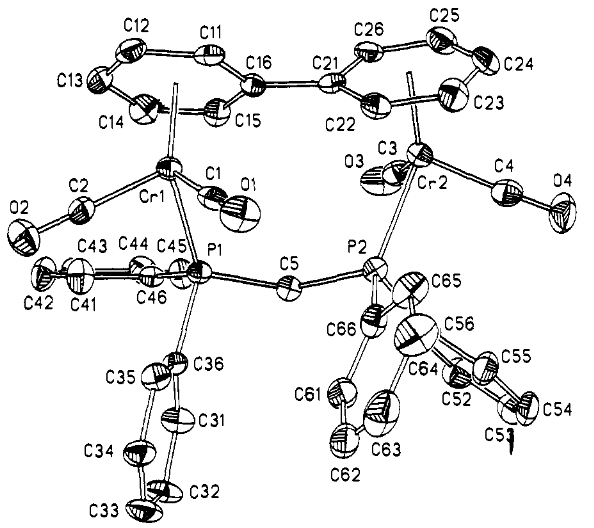

Figure 9. Molecular structure and atom labeling scheme for **8**.

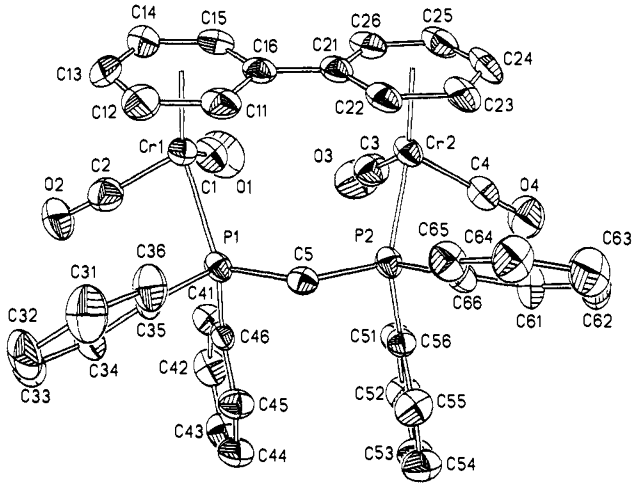

Figure 10. Molecular structure and atom labeling scheme for 8^+.

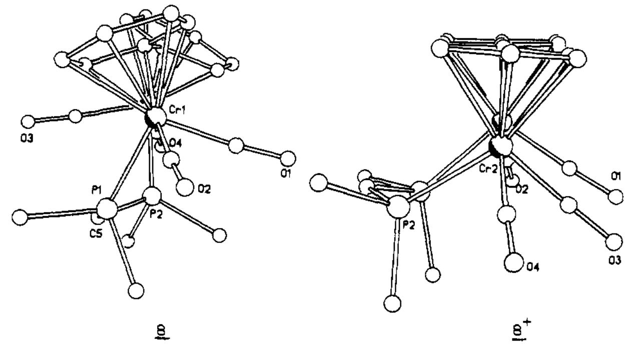

Figure 11. Views of **8** (left) and 8^+ (right) along the Cr⋯Cr vector, emphasizing the difference in the biphenyl torsion angle.

to be on the same side of biphenyl by another bridging ligand (e.g., dppm), a strictly cis orientation is apparently avoided in the neutral complex **8**. Following one-electron oxidation, the biphenyl ligand twist is lost and the two rings are nearly coplanar (torsion angle = 3.7 (4)°) as shown in Figure 11. In Table IV the metrical parameters for **8** and 8^+ are compared.

Accompanying the untwisting of biphenyl is a considerable reduction in the nonbonded Cr⋯Cr separation [**8**, 4.828 (1) Å, 8^+, 4.374 (2) Å], an increase in the Cr–centroid distance [**8**, 1.698 (3) Å (av), 8^+, 1.739 (9) Å (av)], and lengthening of the Cr–carbonyl and Cr–P distances [**8**, Cr–P = 2.321 (6) Å (av), Cr–CO 1.826 (5) Å (av), 8^+, Cr–P = 2.373 (7) Å (av), Cr–CO = 1.85 (1) Å (av). The Cr–centroid and Cr–CO distances in neutral **8** are shorter than those reported for neutral (arene)Cr(CO)$_3$

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(34) (a) Corradini, P.; Allegra, G. *J. Am. Chem. Soc.* **1960**, *82*, 2075. (b) Rees, B.; Coppens, P. *J. Organomet. Chem.* **1972**, *42*, C102. (c) Van Meurs, F.; Van Koningsveld, H. *J. Organomet. Chem.* **1977**, *131*, 423. (d) Andrianov, V. G.; Struchkov, Yu. T.; Baranetzkaya, N. K.; Setkina, V. N.; Kursanov, D. N. *J. Organomet. Chem.* **1975**, *101*, 209.

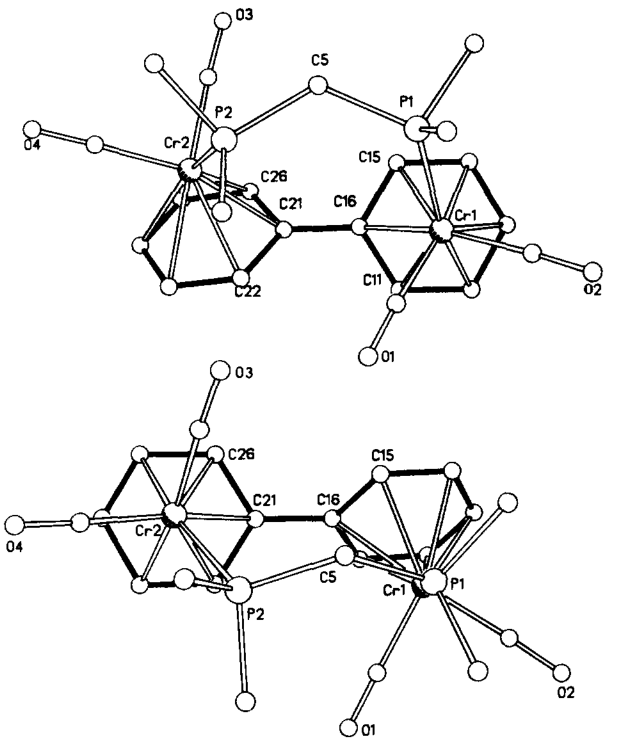

Figure 12. Views of the staggering of the Cr(CO)$_2$P units relative to the arene rings along each Cr–(ring centroid) vector for **8** [Cr(1) view above].

complexes: arene = benzene, Cr–centroid = 1.728 (2) Å and Cr–CO = 1.842 (10) Å,[34b] arene = toluene, Cr–centroid = 1.724 (5) Å.[34c]

The Cr–P distances in **8** and **8$^+$** may be compared to that found in [(methyl benzoate)Cr(CO)$_2$(PPh$_3$)], Cr–P = 2.337 (1) Å.[34d] While the value is nearer to **8** than **8$^+$**, the Cr–P(av) distance in **8** is the shortest Cr–phosphine distance known to us. The Cr–CO distances in the toluene and C$_6$H$_5$CO$_2$CH$_3$ complexes (average 1.824 (4) Å in both) are very similar to those found in **8**.

The lengthening of the Cr–centroid distance on oxidation is contrary to expectations based on EH calculations for [(C$_6$H$_6$)Cr(CO)$_3$][34e] which suggest that the HOMO is slightly antibonding for the Cr–ring bond. However, the effects of the bridging dppm substitution and the curious twisted–untwisted biphenyl transformation undoubtedly perturb the MO levels sufficiently to disallow straightforward conclusions.

Some conclusions about the localization of charge in **8$^+$** may be made. If the metal centers are the primary charge sinks, then the first question is whether a valence-delocalized or – trapped description is more appropriate, i.e., (Cr$_2$)$^{\rm I}$ vs. Cr^0/Cr$^{\rm I}$.[11] Consistent with spectroscopic data, there is no crystallographic evidence to suggest the presence of a trapped-valence state for **8$^+$**. Bond distances to Cr(1) and Cr(2) in **8$^+$** are not significantly different, and the distances between the PF$_6^-$ counterion and the Cr atoms are similar.

The small elongations in the Cr–CO and Cr–P distances in converting **8** to **8$^+$** are consistent with increased charge on the Cr atoms in the latter. Figures 12 and 13 show differences in the staggering of the Cr(CO)$_2$P units relative to the arene rings in the two complexes.

4. [(Benzene)Cr(CO)$_2$]$_2$(μ-dppm) (11). This complex is binuclear but singly bridged, the metals being linked directly by the μ-dppm ligand. Not surprisingly, the cations derived from **11** were less stable than their doubly bridged analogues. However, two anodic waves were discernible due to the successive one-electron oxidations **11**/**11$^+$** and **11$^+$**/**11^{2+}**. CV scans at 273 K of solutions of **11** under dinitrogen gave a fairly reversible first oxidation, but the second anodic wave had a smaller wave height than predicted for a reversible EE process (Figure 14). The current for the second wave was enhanced either at faster sweep rates, at lower temperatures, or under more rigorous conditions.

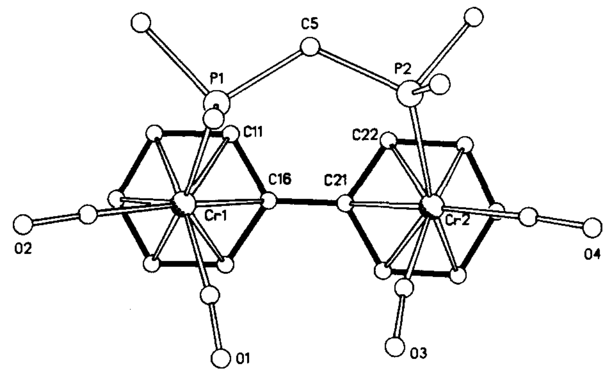

Figure 13. View of the staggering of the Cr(CO)$_2$P units relative to the arene rings along the nearly parallel Cr–(ring centroid) vectors in **8$^+$**.

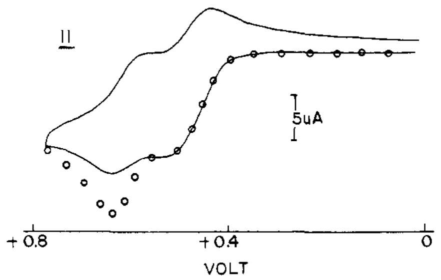

Figure 14. CV scan of [(benzene)Cr(CO)$_2$]$_2$(μ-dppm) (**11**) (3×10^{-4} M in CH$_2$Cl$_2$ at Pt, $T = 273$ K, $v = 0.20$ V s^{-1}). The circles give calculated values of the anodic portion of a EE mechanism using $E_1° = +0.51$ V and $E_2° = +0.67$ V. The lower anodic peak current for the second wave is due to instability of the monocation **11$^+$**.

In a vacuum electrolysis cell at ca. 270 K, currents on the two waves were equal and both processes were reversible. Hence, we can assign the $E°$ values with some confidence as +0.51 and +0.67 V (Table I). No attempts were made to prepare the cations for spectroscopic study. The small but measurable difference (160 mV) in $E°$ values for the first and second oxidations implies some electronic communication of the two halves of the molecule through the dppm-bridging ligand. The $E°$ spread is only slightly lower than that (ca. 200 mV) observed for the dinuclear complex **6** linked only through the phenyl rings.

Discussion

The spectroscopic behavior of the cation having only a biphenyl linkage, (**7$^+$**), stands in clear contrast to that of complexes having both the biphenyl and diphosphino or diarsino linkages (**8$^+$**–**10$^+$**). Both ESR and IR spectra of the former are consistent with a completely localized mixed-valent species, containing one formal Cr(0) and one formal Cr(I) center.

When considering whether there is delocalization between two metal centers, the time scale of the physical technique probing this question is pertinent. The fastest experimental probe we have employed is IR spectroscopy, for which the vibrational time scale ($<10^{-13}$ s) is appropriate. The dinuclear complex **7$^+$** shows complete charge localization on this time scale, with one pair of CO stretches shifting by an amount equal to that of its mononuclear Cr(I) analogue ($\Delta = 53$ and 106 cm^{-1} for the asymmetric and symmetric motions, respectively) and the other pair being unshifted from the original frequencies of the neutral bis-Cr(0) complex. IR shifts have been employed previously to probe mixed-valent charge delocalization.[2,3a,7,8,8s,8y,35] Interpretation of IR shifts for lower energy bands assigned to absorptions involving complex organic ligands (e.g., Cp) rests on an empirical basis since lower frequency infrared bands seldom correspond to simple fundamental modes of vibration.[36] In the present case,

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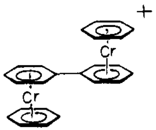
(35) (a) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1973**, *95*, 1086. (b) Schwarzhans, K. E.; Schottenberger, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1983**, *38B*, 1493. (c) Cowan, D. O.; Collins, R. L.; Kaufman, F. *J. Phys. Chem.* **1971**, *75*, 2025. (d) Elschenbroich, Ch.; Stohler, F. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 174.

the relative simplicity of the CO fundamentals and the known connections between ν_{CO} and charge distribution make vibrational spectroscopy a particularly valuable probe.[37]

The ESR spectra of **7**$^+$ probe its electronic structure in ways that differ in two respects from the IR investigations. First, the ESR hyperfine splittings reflect only the electron distribution in the semioccupied molecular orbital (SOMO). That is, the ESR technique probes *spin* distribution rather than *charge* distribution. Second, since the ESR time scale is longer than the IR time scale, our data suggest a lower limit of 10^{-8} s for the residence time of the unpaired electron in the present case. **7**$^+$ in a frozen glass matrix is still a localized mixed-valent complex by these additional criteria, since its hyperfine splittings and *g* values are consistent with those of the mononuclear Cr(I) cations. In this way, **7**$^+$ is seen to be analogous to the (biphenyl)bis(benzenechromium) cation **12**$^+$. Elschenbroich and Heck found evidence for localized mixed-valent behavior for **12**$^+$ in frozen glasses at 77 K.[13] They suggested that the spin localization might occur by ion pairing in the glass, since fluid solutions of **12**$^+$ showed delocalization of the spin over both halves of the complex. This is analogous to the solid-state behavior of the biferrocenium ion B, which may be either localized or delocalized in solid matrices, depending on the temperature and counterion.[11] We have been unsuccessful in obtaining fluid solution ESR spectra of **7**$^+$.



12^+

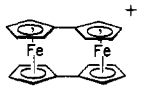
If it is assumed that the signs of the three ^{31}P hyperfine splittings from the glassy spectra are the same, the phosphorus hyperfine interaction is almost purely isotropic. This is consistent with findings for other d^5 phosphino-substituted organometallic radicals,[21,38] which indicate the same magnitude for the phosphorus splitting, ca. 25–30 G. Since this value reveals only a small amount of spin density on phosphorus (≤1% 4s), it does not give a direct probe of the electronic ground state of **7**$^+$. To this end, we were disappointed in not finding ^{53}Cr satellites to help in the electronic assignment. Calculations on the neutral mononuclear (benzene)chromium tricarbonyl[39] indicate that a_1 and e_2 orbitals are the highest lying filled orbitals, so these are the most likely candidates for the SOMO in **7**$^+$. Both orbitals appear to be predominantly metal in character.

A yet longer time scale, that of the electrochemical experiment, gives the only evidence for interaction between the two halves of **7**$^+$. Since two separate one-electron oxidations are observed for **7**, separated by 260 mV, a traditional interpretation would suggest a significant Coulombic interaction between the two redox sites. Although this may well be so, the $E°$ separation is subject to a variety of effects, as will be discussed below.

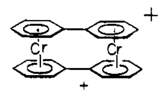
An important factor in determining the magnitude of the electronic interaction between the metals is the degree of twist of the biphenyl linkage. Although the biphenyl dihedral angle of crystalline **6** (and by inference, **7**) is ca. 0°,[34a] it is unlikely to be so in solution. If studies on the arene ligands themselves (i.e., biphenyl and its derivatives) are to be used as a guide, a twist of at least 20° is expected in solution.[40] This would have the effect of partially uncoupling the π-systems of the two rings, as confirmed in the extreme by calculations on the analogue biferrocene in a conformation with perpendicular half-fulvalene rings.[41a] Through-bond coupling via the σ-framework will also be present,[42] although this mechanism is not expected to be too effective in the present case. Whatever the mechanism of charge delocalization, the IR results show that delocalization is not seen on the vibrational time scale. Although it is probable that cations like **7**$^+$, **12**$^+$, and B retain the gross solution geometry implied by the trans structures, the relative ring orientations are open to question and further investigation.

The other singly linked system we have investigated, i.e., **11**, shows only a small $\Delta E°$ value (120 mV). Although spectroscopic investigations of **11**$^+$ were not possible, the $\Delta E°$ value leads us to anticipate that the two metals are in weak electronic communication and that **11**$^+$, like **7**$^+$, is a localized mixed-valent cation. Since the arenes are unlinked in **11**$^+$, its small electronic delocalization should occur via through-bond coupling, via the μ-dppm ligand. A similar value of was $\Delta E°$ was found for dppm-bridged Ru and Os complexes.[43] Spin delocalization through the P–C-H_2–P unit might also occur by a three-centered π-orbital analogous to that observed in acetal radical cations.[44]

The doubly linked systems **8**$^+$–**10**$^+$, on the other hand, indicate complete charge and spin delocalization over both halves of the molecule. In this sense they are analogous to the monocations of bis(fulvalene) diiron, **13**$^+$, and bis(biphenyl)dichromium, **14**$^+$.



13^+



14^+

The former is totally delocalized over the iron and carbon π-framework.[8i,10,41a] The latter shows delocalization over both halves of the molecule in solution ESR studies, but a localized electronic structure in a frozen glass.[13] The greater degree of delocalization in the diiron complex may be due to a direct metal–metal interaction, a factor not considered in the theoretical calculations[41a] on $\mathbf{13}^n$ (n = 0–2) which preceded the revelation[10] that the metal–metal distance in **13**$^+$ is almost 0.4 Å shorter than that in neutral **13**.

If the structure of only neutral **8** with its twisted biphenyl were available, the facile delocalization of **8**$^+$ would be hard to understand. However, the higher degree of biphenyl coplanarity in **8**$^+$ removes any doubt about the possibility of π-delocalization through the phenyl rings in the monocation. Thus, substituting a bridging dppm linkage for the two PR_3 ligands of **7**$^+$ dramatically changes the electronic structure of the mixed-valent cation. Whether this arises simply from a smaller biphenyl twist in **8**$^+$ or from enhancement of the delocalization through the bridging P–CH_2–P group remains to be shown. A synergistic combination of both effects seems most likely at the moment.[41b]

One further question that warrants addressing is how electronic delocalization affects the separation of $E°$ values between two identical redox sites. There are two limiting cases on which there is general agreement. The first (I) assumes no electronic interaction between the two sites (A and A′). This might occur if the bridging group, X, is insulating or if the redox orbitals are or-

I

II

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thogonal. In the second case (II), complete delocalization over the two sites is assumed. In the former, noninteracting case, the $E°$ values for the oxidations of A to A^+ and A′ to $(A')^+$ differ by only a small statistical factor (35.6 mV at 298 K), and in CV studies one reversible-looking wave (of two-electron height) is observed.[8m,46] In the latter extreme of strongly interacting A and A′ sites, $E°$ separations of ca. 0.5 V are observed.[47]

For linked ferrocene systems, the $\Delta E°$ arguments are supported by spectroscopic conclusions in the extremes of large and small $\Delta E°$ values. For example, bis(fulvalene)diiron, **13**, which is highly delocalized, has $\Delta E° = 580$ mV[8c] for the processes $\mathbf{13}/\mathbf{13}^+$ and $\mathbf{13}^+/\mathbf{13}^{2+}$, while 1,2-diferrocenylethane, which forms a metal-localized monocation, has $\Delta E° =$ ca. 40 mV.[8c] Our present dichromium complexes follow this trend, with $\Delta E° \geq 500$ mV for the two oxidations of delocalized **8–10**, but only $\Delta E° = 120$ mV for $\mathbf{11}/\mathbf{11}^+/\mathbf{11}^{2+}$.

However, intermediate values of $\Delta E°$ or relatively small changes in $\Delta E°$ should be viewed with caution in trying to make conclusions about minor changes in delocalization. The actual $\Delta E°$ is affected not only by charge delocalization but also by differences in the change of solvation or ion pairing in the two redox steps and structural changes during or following the electron transfers.[6a,8m,48] These factors have been adequately identified, but not quantified, for binuclear complexes, and further investigations are warranted.

Conclusions

These studies show that a new class of formally mixed-valent homodinuclear cations has been prepared, based on the linkage of (arene)chromium dicarbonyl phosphine units. The monocation $\mathbf{7}^+$ linked only through the biphenyl ligand is a completely localized mixed-valent complex on the vibrational and ESR time scales, with one Cr(I) and one Cr(0) site. The doubly-linked complex **8** displays a severe twist of the biphenyl ligand around the interconnecting C–C bond. The twist relaxes in the monocation of **8**, with the biphenyl moiety having nearly coplanar aryl rings. This structure allows complete delocalization of the charge over the two halves of the molecule. The doubly linked complexes **8** and $\mathbf{8}^+$ thus join a slowly growing but important list of binuclear mixed-valent organometallics that have been structurally characterized in two oxidation states.[8q,r,u,10,11,45] Certainly this structural information will be important in further deciphering the mechanism of intramolecular charge transfer in mixed-valent complexes.

The separations of standard potentials of the two successive one-electron oxidations of these compounds follow the previously observed trend that totally delocalized systems have considerably larger $\Delta E°$ values than those not exhibiting electronic delocalization. However, the quantitative relationship between $\Delta E°$ and electronic delocalization is unclear. Since structural changes are expected to play a role in $\Delta E°$ values, they may contribute significantly to the values for **8** and its analogues, increasing $\Delta E°$ because of the thermodynamic stabilization of $\mathbf{8}^+$ by rotation of the aryl rings toward coplanarity.

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Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atom coordinates, bond distances, and bond angles for **8** and $\mathbf{8}^+$ (13 pages); listings of observed and calculated structure factors for **8** and $\mathbf{8}^+$ (43 pages). Ordering information is given on any current masthead page.

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Synthesis and Structure of 2,4-Bis(2,6-di-*tert*-butyl-4-methylphenoxy)-1,3,2,4-dioxadiphosphetane. An Aryl Phosphenite Dimer

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Abstract: When 2,4,6-tris(2,6-di-*tert*-butyl-4-methylphenoxy)-1,3,5,2,4,6-trioxatriphosphorinane (**1a**) is sublimed at 220 °C under vacuum, a new heterocycle, a 1,3,2,4-dioxadiphosphetane (**3**), is formed. This molecule can be considered a dimer of the aryl phosphenite **2**. Molecule **3** crystallizes in the $P2_1/c$ space group of the monoclinic crystal system with four molecules per unit cell. The X-ray crystal structure of **3** reveals that the P_2O_2 heterocycle exists as a bent rhombus wherein the four ring atoms do not all lie in the same plane. The two 2,6-di-*tert*-butyl-4-methylphenoxy groups are in a cis configuration but the molecule does not possess a plane of symmetry. Using ^{31}P NMR to follow the synthesis of **1a**, we observed the formation and disappearance of **3**. While **3** is stable in THF/$CDCl_3$ solution, it readily converts to **1a** upon addition of amine. These data suggest the intermediacy of **2**.

In a recent publication,[1] we discussed the syntheses, characterizations, and crystal structures of **1a** and **1b**, the first P(III) structures of their kind. These molecules were viewed as the cyclic trimers of the corresponding monomeric aryl phosphenite **2**. However, while the stoichiometry of the reaction leading to **1** suggested the possible intermediacy of **2**, no other experimental data were available. As part of a continuing study to understand

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