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Synthesis, Characterization, and Crystal Structure of the $(\eta^5\text{-}C_5Ph_5)Cr(CO)_3$ Radical

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The reaction between $Cr(CO)_6$ and $Na(C_5Ph_5)$ in refluxing diglyme yields $[Na(diglyme)_{3/2}][(C_5Ph_5)Cr(CO)_3]$, 1. Metathesis of 1 with $[Ph_3P{=}N{=}PPh_3]Cl$ in CH_2Cl_2 yields $[Ph_3P{=}N{=}PPh_3][(C_5Ph_5)Cr(CO)_3]$, 2. Oxidation of 1 by $AgBF_4$ in cold THF under an argon atmosphere produces $(C_5Ph_5)Cr(CO)_3$, 3. Complexes 2 and 3 form a redox pair connected by a quasireversible one-electron process, $E° = -0.69$ V vs ferrocene in CH_2Cl_2, $E° = -0.50$ V in CH_3CN, $k_s = 0.12$ cm/s. ESR spectra of 3 in toluene at 90 K gave a rhombic **g**-tensor with components 2.1366, 2.0224, and 1.9953, consistent with the expected low-spin d^5 electronic configuration. The largest **g**-tensor component was significantly temperature dependent, suggesting an equilibrium between conformations with $^2A'$ and $^2A''$ ground states. Crystals of 2 belong to the space group $P\bar{1}$ with $Z = 2$. The unit-cell parameters are $a = 12.190$ (3) Å, $b = 13.019$ (3) Å, $c = 19.842$ (4) Å, $\alpha = 96.598$ (17)°, $\beta = 103.719$ (17)°, $\gamma = 94.322$ (18)°, and $V = 3021.5$ (11) Å^3 with final values of $R_F = 6.72\%$ and $R_{wF} = 7.57\%$. Crystals of $3{\cdot}C_6H_6$ belong to the space group $P2_1/c$ with $Z = 8$. The unit-cell parameters are $a = 33.307$ (9) Å, $b = 8.978$ (3) Å, $c = 22.702$ (6) Å, $\beta = 91.73$ (2)°, and $V = 6798$ (3) Å^3 with final values of $R_F = 7.69\%$ and $R_{wF} = 7.68\%$.

Introduction

Paramagnetic organometallic complexes have recently received considerable attention because of their demonstrated high reactivity and their proposed roles in a variety of important chemical reactions.[2] One method for isolating such compounds involves replacing a relatively small ligand in an unstable fragment with a larger ligand to prevent formation of a closed-shell compound.[3] One such substitution expected to induce substantial molecular changes is that of the pentaphenylcyclopentadienyl ligand (η^5-C_5Ph_5) used in place of the much smaller cyclopentadienyl ligand (η^5-C_5H_5, Cp). The C_5Ph_5 ligand has been previously shown to impart stability to organometallic radicals.[4]

In 1974, Cotton and co-workers[5] suggested that the unusually long Cr–Cr bond in $[CpCr(CO)_3]_2$ might lead to the generation of $CpCr(CO)_3$ radicals under mild conditions. Work in other groups found that this dimer possessed greatly enhanced reactivity in comparison with the $[CpMo(CO)_3]_2$ dimer.[6-8] There were also numerous studies concerned with characterizing the radical species.[9-15] Recently, Baird[16] and Goh and co-workers[17] attempted to prepare an analogous monomer containing the pentamethylcyclopentadienyl ligand (η^5-C_5Me_5, Cp*).[18] However, the product dimerized in the solid state with an exceed-

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ingly long Cr–Cr bond but in solution exhibited much greater reactivity than the C_5H_5 complex. The extent of monomer formation for these complexes in room-temperature solution (10% for $[CpCr(CO)_3]_2$[9,11] and ca. 90% for $[Cp^*Cr(CO)_3]_2$[15b]) suggested that a still larger cyclopentadienyl ligand would allow isolation of a monomeric species. The isolation of a radical of this type would permit characterization not possible with an equilibrium mixture. In addition, recent ESR work has raised interesting questions about the structure of the $CpCr(CO)_3$ radical doped in $CpMn(CO)_3$ crystals[12a–c] that might be answered by structural characterization of a similar compound.

The photochemical reactivity of $[CpMo(CO)_3]_2$ has been studied extensively[19] with the primary photoproduct in the presence of low-energy light being the $CpMo(CO)_3$ radical.[19a] The latter species can be studied only by fast techniques because recombination occurs at a diffusion-controlled rate.[20] The analogous hydridotris(pyrazolyl)borate (Tp) complexes, $TpM(CO)_3$ (M = Cr,[21] Mo[3c]), have been isolated and characterized. While the Tp and Cp ligands are in some ways similar, differences between them make the isolation of a cyclopentadienyl derivative desirable. Substitution of C_5Ph_5 for C_5H_5 has been shown to generate significant quantities of the $(C_5Ph_5)Mo(CO)_3$ radical in solution; however, this complex also completely dimerizes on crystallization.[22] We now show that the $[(C_5Ph_5)Cr(CO)_3]_n$ system is completely monomeric. The radical is remarkably stable in the absence of air and has been characterized by a number of methods.

Experimental Section

General Data. All reactions of air- and moisture-sensitive materials were performed under an argon atmosphere employing standard Schlenk techniques unless otherwise stated. Solids were manipulated under argon in a Vacuum Atmospheres glovebox equipped with a HE-493 dri-train. Diglyme, toluene, and hexanes were distilled from sodium/benzophenone ketyl under argon. Tetrahydrofuran (THF) and benzene were distilled from potassium/benzophenone ketyl under argon. Dichloromethane and CH_3CN were distilled from CaH_2 under argon. $Na[C_5Ph_5]$ was prepared according to a literature procedure or as described below.[23] NMR solvents were vacuum distilled from CaH_2 and placed under an argon atmosphere. $AgPF_6$, $AgBF_4$, $Cr(CO)_6$ (Strem), diglyme, $[Ph_3P{=}N{=}PPh_3]Cl$ ([PPN]Cl), $CDCl_3$, CD_2Cl_2 (Aldrich), and all other solvents (Fisher) were used without further purification. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

Infrared spectra were recorded on a Nicolet 20 DXB FTIR spectrometer. ^1H NMR spectra were obtained at 200.06 MHz on a Varian XL-200 NMR spectrometer equipped with a Motorola data system upgrade. UV–visible spectra were recorded on a Varian DMS-90 spectrometer.

Electron Spin Resonance Spectra. X-band ESR spectra were obtained using a Bruker ESP300E spectrometer at the University of Bristol. The spectrometer was equipped with a liquid nitrogen Dewar flask and a variable-temperature unit; field-frequency calibration relied on a Hewlett-Packard microwave frequency counter and the Bruker Hall probe, the offset of which was checked from time to time with DPPH. Toluene solutions of $(C_5Ph_5)Cr(CO)_3$ were prepared for ESR spectral studies in several ways, including the use of an argon-filled glovebox, modified Schlenk techniques, and a vacuum line.

Table I. Crystal Data for [PPN][(η^5-C_5Ph_5)Cr(CO)$_3$] (2) and (η^5-C_5Ph_5)Cr(CO)$_3$ (3·C_6H_6)

	$[PPN][(C_5Ph_5)Cr(CO)_3]$	$(C_5Ph_5)Cr(CO)_3{\cdot}C_6H_6$
(a) Crystal Parameters		
formula	$C_{74}H_{55}CrNO_3P_2$	$C_{38}H_{25}CrO_3{\cdot}C_6H_6$
fw	1120.21	659.72
cryst system	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a, Å	12.1903 (28)	33.307 (9)
b, Å	13.0185 (28)	8.978 (3)
c, Å	19.8417 (42)	22.702 (6)
α, deg	96.598 (17)	
β, deg	103.719 (17)	91.73 (2)
γ, deg	94.322 (18)	
V, Å^3	3021.5 (11)	6798 (3)
Z	2	8
cryst dimens, mm	0.36 × 0.37 × 0.46	0.38 × 0.40 × 0.40
cryst color	golden yellow	dark green
D(calc), g cm^{-3}	1.216	1.289
μ(Mo Kα), cm^{-1}	2.81	3.58
temp, K	297	297
(b) Data Collection		
diffractometer	Nicolet R3m	
monochromator	graphite	
radiation (λ, Å)	Mo Kα (0.710 73)	
2θ scan range, deg	4–50	4–42
data collcd (h,k,l)	±15,±16,+24	±33,+8,+22
no. of rflns collcd	10 986	8006
no. of indpt rflns	10 649	7188
no. of indpt obsd rflns ($F_o \geq n\sigma(F_o)$)	6820 (n = 5)	3418 (n = 4)
std rflns	3 std/197 rflns	3 std/197 rflns
var in stds	<1	~2
(c) Refinement		
$R(F)$, %	6.72	7.69
$R(wF)$, %	7.57	7.68
Δ/σ(max)	0.027	0.026
$\Delta(\rho)$, e Å^{-3}	1.061	0.60
N_o/N_v	11.2	9.47
GOF	1.521	1.473

Electrochemistry. Electrochemical data were obtained under a nitrogen atmosphere using drybox procedures previously described.[24] CH_3CN and CH_2Cl_2 were employed as solvents, with a supporting electrolyte of 0.1 M Bu_4NPF_6. Potentials are referred to the ferrocene/ferrocenium (Fc) couple. Conversion to the SCE scale requires addition of +0.46 V (CH_2Cl_2) or +0.40 V (CH_3CN) to these potentials. Data acquisition and treatment was as recently described.[25] All data were obtained with Pt working electrodes, with a Pt bead of ca. 1-mm radius being employed for scan rates below v = 1 V/s and a Pt microdisk (r = 247 μm) being used for 1 V/s < v < 100 V/s. A luggin probe was used to minimize resistance effects.

X-ray Structural Determinations. Crystallographic data are collected in Table I. Crystals of both 2 and 3·C_6H_6 were sealed in capillary tubes, and unit-cell parameters were obtained from the angular settings of 25 reflections. The centrosymmetric triclinic space group $P\bar{1}$ for 2 was initially assumed and was later shown to be correct by the results of least-squares refinement. The space group for 3·C_6H_6 was uniquely determined by systematic absences in the reflection data. Regular crystal size and low μ's for both removed the need for corrections for absorption. The asymmetric unit for 3·C_6H_6 contains two

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Table II. Atomic Coordinates ($\times10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for $[PPN][(C_5Ph_5)Cr(CO)_3]$

	x	*y*	*z*	*U*[a]		*x*	*y*	*z*	*U*[a]
Cr	56.7 (6)	9961.5 (5)	2374.6 (4)	30.1 (2)	C(53)	2445	13741	1789	62 (2)
P(1)	6615 (1)	5033 (1)	3807 (1)	37 (1)	C(54)	2518	12961	1264	65 (3)
P(2)	5013 (1)	6517 (1)	3141 (1)	38 (1)	C(55)	1917	11990	1198	50 (2)
N	5560 (4)	5604 (3)	3511 (2)	49 (2)	C(56)	1242	11798	1657	33 (2)
C(1)	−663	10569	1377	30	C(61)	6605 (3)	3249 (3)	4464 (2)	72 (3)
C(2)	−961	9477	1276	30	C(62)	6166	2255	4521	102 (4)
C(3)	76	8982	1375	28	C(63)	5191	1776	4033	97 (4)
C(4)	999	9776	1536	30	C(64)	4655	2290	3488	88 (3)
C(5)	552	10761	1550	28	C(65)	5094	3284	3431	67 (3)
C(6)	1278 (4)	10310 (4)	3105 (3)	44 (2)	C(66)	6069	3763	3920	42 (2)
O(6)	2066 (4)	10555 (4)	3589 (2)	72 (2)	C(71)	7903 (3)	3899 (2)	3069 (2)	46 (2)
C(7)	−351 (4)	8886 (4)	2798 (2)	37 (2)	C(72)	8659	3800	2642	57 (2)
O(7)	−610 (3)	8187 (3)	3066 (2)	58 (2)	C(73)	9075	4668	2395	60 (2)
C(8)	−676 (4)	10807 (4)	2870 (3)	38 (2)	C(74)	8735	5635	2575	61 (2)
O(8)	−1131 (4)	11363 (3)	3185 (2)	59 (2)	C(75)	7979	5734	3001	51 (2)
C(11)	−2468 (3)	11317 (3)	1486 (2)	49 (2)	C(76)	7562	4866	3248	38 (2)
C(12)	−3227	12057	1349	73 (3)	C(81)	6927 (3)	6163 (3)	5110 (2)	60 (2)
C(13)	−2988	12863	985	81 (3)	C(82)	7570	6751	5728	82 (3)
C(14)	−1989	12927	758	67 (3)	C(83)	8752	6869	5866	89 (4)
C(15)	−1230	12186	895	46 (2)	C(84)	9292	6399	5385	95 (4)
C(16)	−1469	11381	1259	37 (2)	C(85)	8650	5811	4767	74 (3)
C(21)	−2819 (3)	9163 (2)	394 (2)	42 (2)	C(86)	7468	5693	4629	42 (2)
C(22)	−3857	8575	85	56 (2)	C(91)	6263 (3)	8222 (3)	2865 (2)	53 (2)
C(23)	−4192	7724	381	57 (2)	C(92)	6928	9174	3059	66 (3)
C(24)	−3490	7461	986	53 (2)	C(93)	7186	9649	3752	74 (3)
C(25)	−2452	8048	1295	45 (2)	C(94)	6781	9170	4252	82 (3)
C(26)	−2116	8899	1000	34 (2)	C(95)	6116	8218	4058	66 (3)
C(31)	856 (3)	7372 (2)	1766 (1)	41 (2)	C(96)	5858	7744	3364	44 (2)
C(32)	935	6310	1654	49 (2)	C(101)	3833 (3)	6701 (2)	1783 (2)	48 (2)
C(33)	318	5721	1029	59 (3)	C(102)	3471	6387	1063	59 (2)
C(34)	−376	6193	517	62 (2)	C(103)	3903	5544	757	61 (2)
C(35)	−455	7255	630	50 (2)	C(104)	4697	5015	1172	58 (2)
C(36)	161	7844	1254	34 (2)	C(105)	5059	5330	1893	50 (2)
C(41)	3110 (3)	10043 (3)	2117 (1)	59 (2)	C(106)	4627	6173	2198	37 (2)
C(42)	4227	9965	2074	73 (3)	C(111)	3281 (3)	7657 (2)	3417 (2)	49 (2)
C(43)	4444	9461	1467	58 (2)	C(112)	2238	7754	3579	58 (2)
C(44)	3543	9035	904	50 (2)	C(113)	1632	6896	3727	59 (2)
C(45)	2427	9113	948	42 (2)	C(114)	2068	5940	3712	59 (2)
C(46)	2210	9617	1554	35 (2)	C(115)	3111	5843	3549	45 (2)
C(51)	1169 (3)	12577 (2)	2182 (2)	42 (2)	C(116)	3718	6701	3402	37 (2)
C(52)	1770	13548	2248	51 (2)					

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

crystallographically independent, but chemically similar, molecules of the benzene solvated radical species. All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were treated as idealized contributions. Phenyl rings were constrained to be rigid, planar hexagons. Atomic coordinates for 2 and $3{\cdot}C_6H_6$ are listed in Tables II and III, respectively. Bond distances and angles are collected in Tables IV and V, respectively.

All computations used the SHELXTL (5.1) software package (G. Sheldrick, Nicolet (Siemens), Madison, WI).

$Na(C_5Ph_5)$. Method 1. This is a modification of the method of Rausch and co-workers.[23a] Dry toluene (500 mL) was added to a solid mixture of C_5Ph_5H (15.00 g, 33.6 mmol) and $NaNH_2$ (1.25 g, 32.0 mmol). The mixture was refluxed until passage of the reaction solution vapor over red litmus indicated an absence of ammonia. To ensure complete reaction, the solution was refluxed 8–12 h after paper discoloration ceased. Total reflux time was 4 d. The reaction mixture was allowed to cool to room temperature and was filtered through a frit. The resulting solid was stirred in warm benzene (4 × 20 mL, ca. 40–50 °C), filtered out, and dried in vacuo to yield 12.6 g (26.9 mmol, 80%) of $Na(C_5Ph_5)$ as a powdery white solid.

Method 2. Dry THF (50 mL) was added to a solid mixture of C_5Ph_5H (5.00 g, 11.2 mmol) and NaH (0.40 g, 16.8 mmol). The mixture was refluxed overnight, cooled to room temperature, and filtered via cannula to yield a deep yellow solution. The THF was removed in vacuo and the resulting solid dried overnight. The product contains a small amount of residual THF (ca. 5% by ^1H NMR) most of which can be removed by refluxing the pale yellow solid in 20 mL of dry benzene, followed by cooling to room temperature, and drying in vacuo to yield 4.78 g (10.2 mmol, 91%) of $Na(C_5Ph_5)$ as a pale yellow solid.

$[Na(diglyme)_{3/2}][(C_5Ph_5)Cr(CO)_3]$, 1. Dry diglyme (100 mL) was added to a solid mixture of $Cr(CO)_6$ (3.10 g, 14.1 mmol) and $Na(C_5Ph_5)$ (6.01 g, 12.8 mmol). After a 1.5-h reflux, excess $Cr(CO)_6$ was sublimed into the reflux condenser with a heat gun. Note: Prolonged refluxing of the reaction solution leads to product decomposition. The condenser was removed, and the hot solution was filtered via cannula into a second flask. Hexanes (20 mL) were added, and the solution was swirled to generate a homogeneous solution. After cooling to −15 °C overnight, the solution was filtered and the resulting crystals were washed with hexanes (10 mL), to yield 8.09 g (10.0 mmol, 78%) of dark yellow crystals of 1. Occasionally, a black material coprecipitates with the product. It can be removed by recrystallization from diglyme/hexanes. Mp: 228–230 °C. ^1H NMR ($CDCl_3$): δ 3.34 (s, 9, CH_3), 3.50–3.65 (m, 12, CH_2), 6.90–7.20 (m, 25, C_6H_5). Anal. Calcd for $C_{94}H_{92}Cr_2Na_2O_{15}$: C, 70.05; H, 5.75. Found: C, 69.62; H, 6.07.

$[PPN][(C_5Ph_5)Cr(CO)_3]$, 2. $[Na(diglyme)_{3/2}][(C_5Ph_5)Cr(CO)_3]$ (1.00 g, 1.24 mmol) and [PPN]Cl (0.69 g, 1.2 mmol) were each dissolved in 5 mL of CH_2Cl_2. The solutions were combined, stirred for 20 min, filtered to remove the NaCl precipitate, and dried in vacuo. The resulting yellow powder was stirred with 5 mL of acetone for 5 min to dissolve any residual [PPN]Cl. The acetone was removed by cannula filtration, and the solid was dried in vacuo. The resulting solid was dissolved in CH_2Cl_2 (15 mL) and layered with an equal volume of hexanes. The layers were allowed to combine in the dark producing large orange blocks of 2 in 70% yield (0.97 g, 0.87 mmol). Mp: 241–

Table III. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters (Å^2 $\times$ 10^3) for $(C_5Ph_5)Cr(CO)_3\cdot C_6H_6$

	x	y	z	U^a		x	y	z	U^a
Cr	1213.2 (5)	6161.7 (21)	5080.2 (8)	43.0 (7)*	C(6′)	3224 (4)	8530 (14)	8213 (5)	54 (5)*
Cr′	3786.8 (5)	8300.5 (20)	8272.4 (8)	38.4 (7)*	O(6′)	2890 (3)	8657 (11)	8150 (4)	84 (4)*
C(1)	1214 (3)	4067 (12)	5578 (5)	33 (4)*	C(7′)	3867 (3)	9914 (16)	8786 (5)	51 (5)*
C(2)	1597 (3)	4734 (12)	5681 (4)	34 (4)*	O(7′)	3908 (3)	10887 (11)	9100 (4)	95 (5)*
C(3)	1783 (3)	4860 (12)	5125 (5)	36 (4)*	C(8′)	3778 (3)	9649 (15)	7662 (5)	52 (5)*
C(4)	1521 (3)	4209 (11)	4681 (5)	36 (4)*	O(8′)	3757 (3)	10511 (10)	7284 (4)	80 (4)*
C(5)	1166 (3)	3734 (11)	4975 (5)	35 (4)*	C(11′)	3415 (2)	6293 (7)	6938 (3)	50 (3)
C(6)	1093 (4)	7572 (16)	5643 (5)	60 (6)*	C(12′)	3274	5720	6400	66 (4)
O(6)	1003 (3)	8470 (12)	5976 (4)	107 (5)*	C(13′)	3499	4661	6105	59 (4)
C(7)	1426 (3)	7801 (14)	4689 (5)	58 (5)*	C(14′)	3865	4175	6348	58 (4)
O(7)	1570 (3)	8812 (11)	4477 (4)	89 (5)*	C(15′)	4006	4748	6886	52 (3)
C(8)	681 (4)	6472 (14)	4880 (5)	58 (5)*	C(16′)	3781	5807	7182	31 (3)
O(8)	334 (3)	6635 (11)	4777 (5)	102 (5)*	C(21′)	3079 (2)	5336 (7)	8758 (3)	43 (3)
C(11)	529 (2)	3744 (8)	5991 (3)	56 (4)	C(22′)	2744	4425	8818	61 (4)
C(12)	279	3094	6400	69 (4)	C(23′)	2708	3112	8492	67 (4)
C(13)	442	2215	6854	70 (4)	C(24′)	3007	2711	8106	64 (4)
C(14)	855	1986	6899	77 (4)	C(25′)	3342	3622	8045	45 (3)
C(15)	1106	2636	6490	55 (4)	C(26′)	3378	4934	8372	36 (3)
C(16)	942	3515	6036	32 (3)	C(31′)	3835 (2)	4565 (7)	9594 (3)	50 (3)
C(21)	1565 (2)	5882 (8)	6691 (3)	52 (3)	C(32′)	3783	4218	10186	63 (4)
C(22)	1740	6165	7245	66 (4)	C(33′)	3833	5318	10616	65 (4)
C(23)	2129	5674	7379	68 (4)	C(34′)	3935	6765	10454	55 (4)
C(24)	2343	4900	6958	68 (4)	C(35′)	3987	7112	9862	42 (3)
C(25)	2168	4617	6403	52 (4)	C(36′)	3937	6012	9432	34 (3)
C(26)	1779	5108	6270	35 (3)	C(41′)	4870 (2)	6718 (6)	9337 (3)	44 (3)
C(31)	2343 (2)	6775 (7)	5207 (3)	47 (3)	C(42′)	5190	7248	9686	52 (4)
C(32)	2736	7207	5100	62 (4)	C(43′)	5333	8692	9605	69 (4)
C(33)	2990	6247	4805	54 (4)	C(44′)	5154	9606	9174	54 (4)
C(34)	2852	4855	4617	56 (4)	C(45′)	4834	9077	8826	45 (3)
C(35)	2459	4423	4724	45 (3)	C(46′)	4691	7633	8907	36 (3)
C(36)	2205	5383	5019	39 (3)	C(51′)	4502 (2)	8119 (8)	6969 (3)	42 (3)
C(41)	1771 (2)	5130 (7)	3705 (3)	50 (3)	C(52′)	4795	8451	6563	52 (3)
C(42)	1857	4866	3117	56 (4)	C(53′)	5195	8087	6688	55 (4)
C(43)	1781	3471	2868	65 (4)	C(54′)	5302	7392	7219	59 (4)
C(44)	1618	2339	3207	65 (4)	C(55′)	5010	7061	7625	41 (3)
C(45)	1532	2602	3795	52 (3)	C(56′)	4610	7425	7500	30 (3)
C(46)	1609	3997	4044	41 (3)	Cs(1)^b	602 (3)	7008 (12)	2340 (4)	95 (5)
C(51)	626 (2)	3403 (7)	4185 (3)	56 (4)	Cs(2)	769	6378	2852	90 (5)
C(52)	321	2554	3919	75 (4)	Cs(3)	885	7287	3326	73 (4)
C(53)	223	1168	4153	76 (4)	Cs(4)	834	8827	3286	93 (5)
C(54)	431	632	4652	66 (4)	Cs(5)	667	9456	2774	96 (5)
C(55)	736	1482	4917	59 (4)	Cs(6)	551	8547	2300	89 (5)
C(56)	834	2867	4684	35 (3)	Cs(7)	2099 (4)	5334 (12)	1439 (5)	127 (6)
C(1′)	3928 (3)	6255 (11)	7777 (4)	30 (4)*	Cs(8)	1978	4690	903	115 (6)
C(2′)	3742 (3)	5854 (11)	8324 (5)	33 (4)*	Cs(9)	2257	3945	564	121 (6)
C(3′)	4005 (3)	6334 (11)	8800 (4)	32 (4)*	Cs(10)	2656	3846	761	135 (7)
C(4′)	4342 (3)	7057 (11)	8554 (4)	24 (4)*	Cs(11)	2777	4490	1297	144 (7)
C(5′)	4306 (3)	7004 (11)	7931 (4)	26 (4)*	Cs(12)	2498	5235	1636	140 (7)

[a] An asterisk indicates an equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor. [b] Cs refers to the lattice benzene molecules.

Table IV. Bond Lengths (Å) in [PPN][$(C_5Ph_5)Cr(CO)_3$] and $(C_5Ph_5)Cr(CO)_3\cdot C_6H_6$

		$(C_5Ph_5)Cr(CO)_3$	
	[PPN][$(C_5Ph_5)Cr(CO)_3$]	conformer A	conformer B
Cr–C(1)	2.227 (1)	2.194 (11)	2.212 (10)
Cr–C(2)	2.229 (1)	2.244 (10)	2.205 (10)
Cr–C(3)	2.240 (1)	2.233 (10)	2.243 (10)
Cr–C(4)	2.236 (1)	2.237 (11)	2.240 (9)
Cr–C(5)	2.214 (1)	2.198 (11)	2.244 (9)
Cr–CNT	1.867 (1)	1.860 (3)	1.863 (3)
Cr–C(6)	1.802 (5)	1.852 (14)	1.888 (13)
Cr–C(7)	1.816 (5)	1.870 (12)	1.873 (14)
Cr–C(8)	1.818 (5)	1.842 (13)	1.839 (13)
C(1)–C(2)	1.427 (1)	1.425 (14)	1.452 (14)
C(2)–C(3)	1.446 (1)	1.427 (15)	1.438 (14)
C(3)–C(4)	1.422 (1)	1.440 (15)	1.427 (14)
C(4)–C(5)	1.436 (1)	1.441 (15)	1.415 (13)
C(1)–C(5)	1.434 (1)	1.404 (15)	1.461 (13)
C(6)–O(6)	1.180 (6)	1.151 (17)	1.125 (15)
C(7)–O(7)	1.169 (7)	1.140 (16)	1.134 (17)
C(8)–O(8)	1.160 (7)	1.182 (16)	1.157 (16)

242 °C. Anal. Calcd for $C_{74}H_{55}CrNO_3P_2$: C, 79.34; H, 4.95. Found: C, 79.08; H, 5.08.

Table V. Bond Angles (deg) in [PPN][$(C_5Ph_5)Cr(CO)_3$] and $(C_5Ph_5)Cr(CO)_3\cdot C_6H_6$

		$(C_5Ph_5)Cr(CO)_3$	
	[PPN][$(C_5Ph_5)Cr(CO)_3$]	conformer A	conformer B
C(6)–Cr–C(7)	88.7 (2)	83.3 (6)	94.7 (5)
C(7)–Cr–C(8)	89.9 (2)	98.2 (5)	87.6 (6)
C(6)–Cr–C(8)	86.0 (2)	80.8 (6)	83.3 (5)
Cr–C–O (avg.)	178.9 (5)	176.5 (11)	177.6 (11)
P(1)–N–P(2)	150.9 (3)		

$(C_5Ph_5)Cr(CO)_3\cdot C_6H_6$, 3·$C_6H_6$. Cold, freshly distilled THF (10 mL, −78 °C) was added with stirring to a solid mixture of [Na(diglyme)$_{3/2}$][$(C_5Ph_5)Cr(CO)_3$] (1.00 g, 1.24 mmol) and $AgBF_4$ (0.24 g, 1.23 mmol) cooled in a −78 °C bath. The solution was initially yellow-green and turned deep blue on warming. When the temperature exceeded 0 °C (ca. 2 h), the solution was filtered through Celite and the solvent was removed in vacuo. The dark blue-green solid was dissolved in warm benzene (20 mL, 40 °C), and the solution was combined with 20 mL of hexanes and cooled to −15 °C overnight to yield 0.52 g (64%) of dark blue-green

3$\cdot$C$_6$H$_6$. Mp: 205 °C dec. Visible λ_{max} (C$_6$H$_6$): 611 nm. Anal. Calcd for $C_{44}H_{31}CrO_3$: C, 80.11; H, 4.74. Found: C, 79.76; H, 5.11.

Results and Discussion

Synthesis and Reactivity. Reaction of $Cr(CO)_6$ and $Na(C_5Ph_5)$ in refluxing diglyme yields bright yellow, crystalline $[Na(diglyme)_{3/2}][(C_5Ph_5)Cr(CO)_3]$, **1**, in 75% yield (eq 1). This procedure is similar to that used by

$$Cr(CO)_6 + Na(C_5Ph_5) \xrightarrow[\Delta]{\text{diglyme}} [Na(diglyme)_{3/2}][(C_5Ph_5)Cr(CO)_3] \quad (1)$$

Slocum and co-workers to prepare the analogous lithio compound ($[Li(diglyme)_3][(C_5Ph_5)Cr(CO)_3]$).[26,27] The stoichiometry of **1** was established by ^{1}H NMR spectroscopy and elemental analysis. Solutions of **1** decompose in the air within minutes, while the solid requires several hours for significant decomposition to occur. Complex **1** is soluble in THF, CH_2Cl_2, and CH_3CN. It also dissolves in benzene, although, if the solution is sufficiently concentrated, a yellow solid (presumably diglyme-free $Na[(C_5Ph_5)Cr(CO)_3]$) precipitates. Unlike $Na[CpCr(CO)_3]$,[6b] $[Na(diglyme)_{3/2}][(C_5Ph_5)Cr(CO)_3]$ does not react with excess (50 molar equiv) acetic acid in THF solution.

The $Na(C_5Ph_5)$ used in the synthesis of **1** was prepared by three routes. The first was the method of Rausch and co-workers[23a] (eq 2), which works well in our hands.

$$C_5Ph_5H + NaNH_2 \xrightarrow[\Delta]{\text{toluene}} Na(C_5Ph_5) + NH_3 \quad (2)$$

Unfortunately, it required relatively large solvent volumes (ca. 100 mL of toluene/g of $Na(C_5Ph_5)$), which made scaling up the reaction difficult. The reaction was modified by increasing the reactant to solvent ratio 3-fold with a proportional increase in reaction time. Unfortunately, the resultant product required numerous benzene washes to remove unreacted C_5Ph_5H.[28] A different modification involved employing THF as the reaction solvent (eq 3).

$$C_5Ph_5H + NaH \xrightarrow[\Delta]{\text{THF}} Na(C_5Ph_5) + H_2 \quad (3)$$

This method has several advantages over the previously described methods: (1) much smaller solvent volumes are required, (2) the reaction time is significantly reduced, (3) contamination by residual deprotonating agent is not possible, and (4) reaction completion is easily discerned (the reactant C_5Ph_5H is only poorly soluble in refluxing THF while $Na(C_5Ph_5)$ is quite soluble). We find this method to be the most convenient method of preparing large quantities (>5 g) of $Na(C_5Ph_5)$.

Metathesis of **1** with [PPN]Cl in CH_2Cl_2 solution yields $[PPN][(C_5Ph_5)Cr(CO)_3]$, **2**, in 70% yield as large, orange blocks (eq 4). Complex **2** is soluble in dichloromethane but poorly soluble in other solvents. Solid **2** shows no evidence of decomposition after exposure to the air for 7 days, while solutions of it decompose in several minutes.

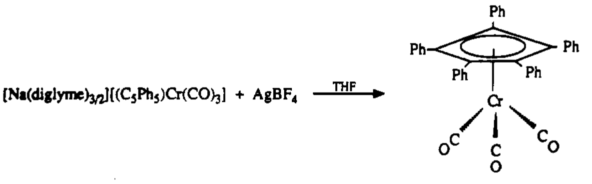
Table VI. Infrared Spectral Data for $(C_5R_5)Cr(CO)_3{}^{0/-}$ Complexes

complex	solvent	ν(C≡O), cm^{-1} [a]	ref
$Na[(C_5H_5)Cr(CO)_3]$	THF	1897, 1793, 1743	30
$[Na(HMPA)_x][(C_5H_5)Cr(CO)_3]$[b]	THF	1895, 1778	30
$[Na(dg)_{3/2}][(C_5Ph_5)Cr(CO)_3]$[c]	CH_3CN	1892, 1783	this work
	CH_2Cl_2	1891, 1783	this work
	THF	1896, 1802, 1757	this work
$[PPN][(C_5Ph_5)Cr(CO)_3]$[d]	CH_3CN	1893, 1783	this work
	CH_2Cl_2	1891, 1781	this work
	THF	1895, 1792	this work
	mull	1888, 1790, 1775	this work
$(C_5H_5)Cr(CO)_3$	toluene	2013, 1895	9, 31
	CO matrix	1986, 1910, 1902	32
$(C_5Me_5)Cr(CO)_3$	toluene	1994, 1895	16
$(C_5Ph_5)Cr(CO)_3$	toluene	2005, 1901	this work
	THF	2005, 1897	this work
	mull	1998, 1885	this work

[a] All bands are strong. [b] HMPA = hexamethylphosphoramide. [c] dg = diglyme. [d] PPN = bis(triphenylphosphine)ammonium cation.

$$[Na(diglyme)_{3/2}][(C_5Ph_5)Cr(CO)_3] + [PPN]Cl \xrightarrow{CH_2Cl_2} [PPN][(C_5Ph_5)Cr(CO)_3] \quad (4)$$

Oxidation of THF solutions of **1** by either $AgBF_4$ or $AgPF_6$ under an argon atmosphere rapidly produces deep blue-green $(C_5Ph_5)Cr(CO)_3$, **3**, in a 64% isolated yield (eq 5). The use of freshly distilled THF is important since



(5)

the presence of even minute amounts of peroxide leads to complete decomposition of the product in seconds to hours. Solutions of **3** in freshly distilled THF are stable for over 1 week. Complex **3** dissolves in THF, C_6H_6, toluene, and CH_2Cl_2. It is very air-sensitive, both in solution and as a solid. $(C_5Ph_5)Cr(CO)_3$ rapidly substitutes small Lewis bases, such as PMe_3, $P(OMe)_3$, and ^{t}BuNC, for CO to yield crystalline products.[29]

Infrared Spectra. Infrared spectra of complexes **1**–**3** were obtained in a variety of solvents and in the solid state (Table VI). The results obtained for anions **1** and **2** are similar to those reported by Darensbourg and co-workers for the $CpCr(CO)_3{}^-$ ion.[30] In coordinating solvents, the Na$^+$ ion in **1** does not associate with the $(C_5Ph_5)Cr(CO)_3{}^-$ ion, and a spectrum consistent with C_{3v} symmetry is obtained. In THF, the Na$^+$ ion appears to associate with a carbonyl ligand, lowering the apparent molecular symmetry and splitting the Cr–CO E band. Use of the noncoordinating PPN$^+$ ion results in solvent-independent spectra, similar to the spectra of **1** in coordinating solvents.

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(28) The similar solubility of C_5Ph_5H to some subsequent products can make its separation from those products in a later step difficult. Thus, complete removal of C_5Ph_5H in this step is recommended.

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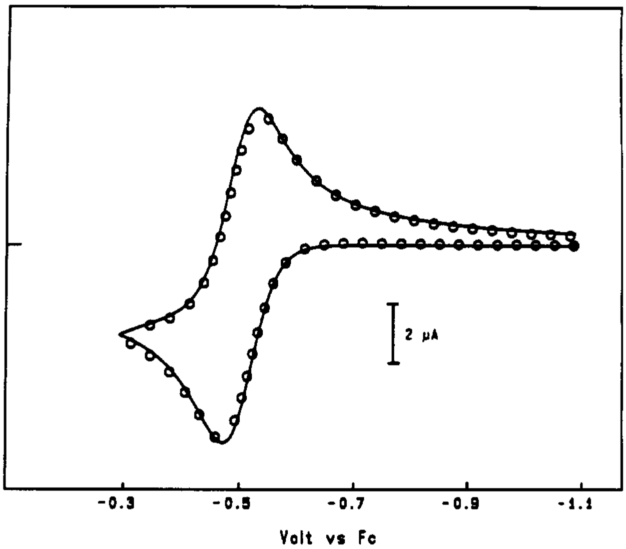

Figure 1. Circles: Cyclic voltammetry scan of 0.8 mM **2** in CH_3CN/0.1 M Bu_4NPF_6 with charging current subtracted (v = 0.3 V/s; T = 296 K; working electrode = 0.7-mm Pt disk). Solid line: Finite difference simulation of quasireversible charge-transfer, chemically reversible system (n = 1e$^-$; k_s = 0.12 cm/s; diffusion coefficient = 8.5 × 10^{-6} cm^2/s; α = 0.5).

The infrared spectrum of (C_5Ph_5)Cr(CO)$_3$, **3**, in toluene solution shows two absorptions of intensity comparable to **2** but shifted ca. 110 cm^{-1} to higher energy. This is consistent with a one-electron oxidation and retention of the molecular symmetry. Thus, (C_5Ph_5)Cr(CO)$_3$ exists exclusively as a monomer in solution. The Nujol mull IR spectrum of **3** displays two absorptions nearly superimposable on the solution spectrum. In contrast, the spectrum of [CpCr(CO)$_3$]$_2$ displays four absorptions. The fact that the mull spectrum has only two absorptions also suggests the complex is monomeric in the solid state.

Cyclic Voltammetry of 2. The oxidation of [PPN][(C_5Ph_5)Cr(CO)$_3$], **2**, was investigated in CH_2Cl_2 and CH_3CN by cyclic voltammetry (CV, Figure 1). In both cases a diffusion-controlled, one-electron oxidation was observed, $E°$ = −0.69 V vs Fc in CH_2Cl_2 and −0.50 V in CH_3CN. No deviation from chemical reversibility was noted with scan rates above v = 0.05 V/s, consistent with the above noted high stability of the neutral radical.

Given the relatively high resistance of CH_2Cl_2 solutions, quantitative fits of CV curves to theory were restricted to the data obtained from CH_3CN solutions, the range of scan rates being 0.3–100 V/s. Typical values of the peak potential difference, ΔE_p, were 78 mV with v = 10 V/s and 102 mV with v = 50 V/s. Finite difference digital simulations were observed to be consistent with experiment for a quasireversible one-electron-transfer reaction uncomplicated by coupled chemical reactions. The electron-transfer coefficient, α, is 0.50 and the standard heterogeneous charge-transfer rate, k_s, is 0.12 cm/s on the basis of these fits. The simulations assumed equal diffusion coefficients (8.5 × 10^{-6} cm^2/s) for both **2** and **3**. The apparent k_s value required to fit the experimental curves was essentially unchanged over more than 2 orders of magnitude in scan rate. This suggests that the reported value is not significantly affected by errors arising from *iR* loss. Such errors should have become more important at high sweep rates owing to the increasingly important charging current background, and no such effect was observed.

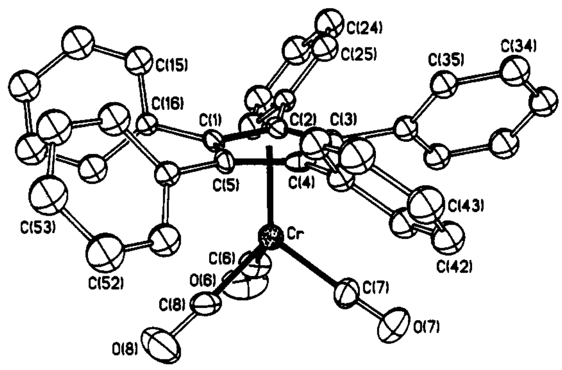

Figure 2. Molecular structure and labeling scheme for (C_5Ph_5)Cr(CO)$_3^{0,-}$.

The k_s value is about the same as that reported[33] for an analogous π-hydrocarbon complex of a metal carbonyl fragment, (η^4-C_8H_8)Fe(CO)$_3^{0/-}$, but at least 1 order of magnitude below that reported for the oxidation of ferrocene.[34] We ascribe no special significance to the lower k_s value of **2**/**3**, since, among other reasons, the electrode dependence of the value was not tested.[35] Among the possible factors limiting the charge-transfer rate are solvent dynamics and ion-pairing changes.

The voltammetry of **2** was investigated in CH_2Cl_2 as a function of temperature, using [**2**] = 1.2 mM. The purpose of this experiment was to search for evidence of dimerization at low temperatures, in light of a report showing that the metal–metal bonded dimer [CpCr(CO)$_3$]$_2$ is favored under such conditions.[12d] At temperatures as low as 223 K, no deviation from chemical reversibility was noted for the oxidation of **2**, showing that no dimerization occurred after its one-electron oxidation to **3**. Hence, it can be concluded that the 17-electron radical **3** is quite robust with respect to dimerization, even at significantly reduced temperatures.

The $E°$ value for **2** $\rightleftarrows$ **3** + e$^-$ in CH_2Cl_2, −0.69 V, may be compared with that reported for the Cp analogue in the same medium, −0.83 V.[12d] The shift of +140 mV in the pentaphenylcyclopentadienyl complex is consistent with previous observations that the phenyl substituents result in a moderate stabilization of low oxidation states in η^5-C_5R_5 complexes.[4e,f]

Molecular Structure. Crystal structures of [PPN][(C_5Ph_5)Cr(CO)$_3$] and (C_5Ph_5)Cr(CO)$_3$·C_6H_6 are displayed in Figure 2. Bond distances and angles are listed in Tables IV and V. For both compounds, bond lengths within the cyclopentadienyl ligand are typical for a coordinated C_5Ph_5 ligand. The phenyl ring torsion angles (Table VII) do not appear to vary systematically between the compounds. The (C_5Ph_5)Cr(CO)$_3$ radical crystallizes with two conformers in the unit cell with the torsion angles and the OC–Cr–CO angles representing the only significant differences between them. These results, in conjunction with the reports of other C_5Ph_5-containing complexes,[23,26c,36]

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[33] Tulyathan, B.; Geiger, W. E. *J. Electroanal. Chem.* **1980**, *109*, 325.

[34] (a) Wipf, D. O.; Kristensen, E. W.; Deakin, M. R.; Wightman, R. M. *Anal. Chem.* **1988**, *60*, 306. (b) Gennett, T.; Milner, D. F.; Weaver, M. J. *J. Phys. Chem.* **1985**, *89*, 2787. (c) Gennett, T.; Weaver, M. J. *J. Electroanal. Chem.* **1985**, *186*, 179.

[35] See: Geiger, W. E. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; Wiley: New York, 1985; Vol. 33, pp 291–297.

[36] (a) Heeg, M. J.; Herber, R. H.; Janiak, C.; Zuckerman, J. J.; Schumann, H.; Manders, W. F. *J. Organomet. Chem.* **1988**, *346*, 321. (b) Field, L. D.; Hambley, T. W.; Lindall, C. M.; Masters, A. F. *Polyhedron* **1989**, *8*, 2425.

Table VII. Phenyl Ring Torsion Angles (deg)

		$(C_5Ph_5)Cr(CO)_3$	
phenyl no.	$[PPN][(C_5Ph_5)Cr(CO)_3]$	conformer A	conformer B
1	42.0	52.8	66.0
2	51.8	47.6	49.4
3	52.7	52.6	48.2
4	61.5	46.6	51.7
5	59.3	54.3	43.3
av	53.5	50.8	51.7

Table VIII. ESR Parameters for $(C_5Ph_5)Cr(CO)_3$

T, K	g_1	g_2	g_3
77	2.1387 (4)	2.0225 (3)	1.9952 (2)
90	2.1366 (3)	2.0224 (2)	1.9953 (2)
100	2.1345 (4)	2.0224 (3)	1.9954 (2)
110	2.1327 (5)	2.0220 (4)	1.9954 (2)
130		2.0214 (16)	1.9957 (3)

suggest that intermolecular packing forces are the dominant factor in determining torsion angles in coordinated C_5Ph_5 ligands.

In each case, the metal is centered 1.86 Å beneath the C_5 ring. In the anion **2**, the OC–Cr–CO angles are close to 90°, and similar to those predicted[37] for and found in isoelectronic $CpMn(CO)_3$[38] and $Cp^*Mn(CO)_3$.[12c] The corresponding angles in $[Me_4N][CpCr(CO)_3]$ are also close to 90°; however, they differ slightly from the expected values, due to interaction between one CO and the Me_4N^+ cation.[39]

Two significant differences between the structures of **2** and **3**·C_6H_6 include changes in the Cr–C(O) bond lengths and the OC–Cr–CO bond angles. As expected, oxidation of the anion leads to a lengthening of the Cr–C(O) bond. While the OC–Cr–CO bond angles in the anion are very close to 90°, those in the radical are significantly different. Calculations by Fortier and co-workers[12c] predict two ground-state configurations ($^2A'$ and $^2A''$) of similar energy for $CpCr(CO)_3$. The calculations predict that the OC–Cr–CO angles should differ considerably from 90°, which is observed for the conformers of $(C_5Ph_5)Cr(CO)_3$. It is possible that both predicted ground-state configurations are present for $(C_5Ph_5)Cr(CO)_3$ and correspond to the two observed conformers.

ESR Spectra. The spectrum of $(C_5Ph_5)Cr(CO)_3$ in a toluene glass in the temperature range 77–110 K shows the characteristic pattern expected for a rhombic **g**-tensor. The measured **g**-tensor components are given in Table VIII. The low-field feature (width at half-height ca. 30 G at 90 K) (Figure 3) broadens as the temperature increases and disappears into the baseline above 120 K. The central feature (ca. 16 G wide at 90 K) also broadens but remains detectable up to about 150 K; the high-field feature (ca. 12 G wide at 90 K) remains well-defined up to about 140 K but broadens at higher temperatures. The spectrum was found to be very sensitive to the quality of the glass. Rapidly frozen samples often showed many extra features; however, when the sample was thawed and slowly recooled, the extra features disappeared, leaving only the canonical three.

The experimental **g**-tensor is characteristic of a low-spin d^5 system[40] and is very similar to that obtained for

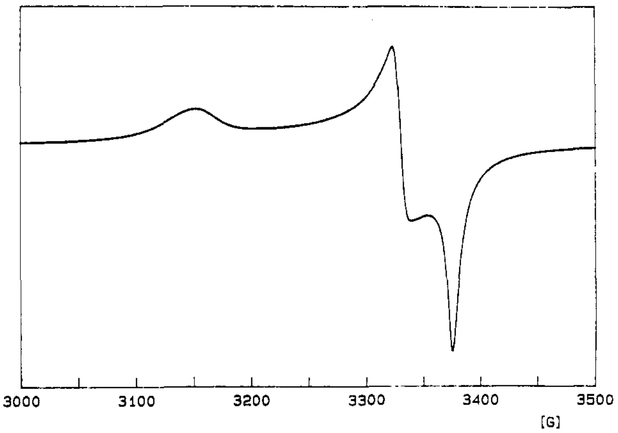

Figure 3. X-Band ESR spectrum of $(C_5H_5)Cr(CO)_3$ in toluene at 90 K.

$CpCr(CO)_3$ (2.1339, 2.0353, 1.9969)[12b] and $(C_5Me_5)Cr(CO)_3$ (2.1215, 2.0192, 1.9973).[12c] Fortier and co-workers[12c] concluded that the ground state of $CpCr(CO)_3$ is $^2A'$, whereas that of $(C_5Me_5)Cr(CO)_3$ is $^2A''$. The spectroscopic distinction between the two symmetries lies in the orientations of the **g**-tensor principal axes relative to the molecular axes, information not available from a frozen-solution spectrum.

As shown in Table VIII, g_1 is significantly temperature-dependent, whereas g_2 and g_3 remain constant within the experimental uncertainty. This behavior suggests that, in frozen toluene, there is a temperature-dependent equilibrium between the conformations giving $^2A'$ and $^2A''$ ground states. At the temperature of our experiments, the lifetimes of these conformations are apparently long enough that a superposition of the spectra of the two conformers is observed. At higher temperatures, the lifetimes decrease and the spectrum broadens and eventually becomes undetectable. In order to rationalize the observation of a single low-field feature, the centers of the two components must differ by less than the line width, ca. 30 G, suggesting that the g_1 values for the two conformers differ by no more than about 0.02. Furthermore, the energy difference must be quite small, on the order of 1–2 kJ/mol, in order to account for the appearance of both conformers and for the temperature coefficient.

Although the frozen-solution spectrum is undectable above 150 K, spectra of liquid solutions showed a wide range of features which depended to some extent on the method of sample preparation. The isotropic features as a group always had an integrated intensity less than 1% of that of the frozen $(C_5Ph_5)Cr(CO)_3$ spectrum and are apparently all due to decomposition products. The isotropic features include the following: (1) A 1:1:1 triplet is found at $\langle g \rangle = 1.9830 \pm 0.0003$,[41] $\langle a \rangle = 5.00 \pm 0.07$ G; this resonance appeared only for samples which were prepared under or otherwise exposed to N_2. This result is reminiscent of the $\langle g \rangle = 1.98$ resonance at first assigned to $TpMo(CO)_3$ by Curtis and co-workers.[42] Isotropic g-values less than g_e are inconsistent with low-spin d^5 systems but are expected for the +3 or +5 oxidation states

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[37] Litchenberger, D. L.; Fenske, R. F. *J. Am. Chem. Soc.* **1976**, *98*, 50.

[38] Berndt, A. F.; Marsh, R. E. *Acta Crystallogr.* **1963**, *16*, 118.

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[41] Uncertainties quoted here are standard deviations from the mean of g-values measured for about 40 spectra of six different samples in the temperature range 200–300 K.

[42] Shiu, K.-B.; Curtis, M. D.; Huffman, J. C. *Organometallics* **1983**, *2*, 936.

of chromium or molybdenum. It is likely that both our triplet and Curtis' singlet correspond to minor oxidation products. (2) Single resonances are found at $\langle g \rangle = 2.005 \pm 0.001$; these features were quite sharp and are consistent with organic radicals with no hyperfine structure, possibly including C_5Ph_5. (3) A resonance at $\langle g \rangle = 2.026 \pm 0.002$ or 2.020 ± 0.001 was seen in most samples; however, the two features never occurred together. (4) Similarly, a resonance occurred at $\langle g \rangle = 2.0144 \pm 0.0002$ or 2.0116 ± 0.0003 in many samples but never at both positions. (5) Finally, one sample showed a broad feature at $\langle g \rangle = 2.04$.

The feature at $\langle g \rangle = 2.026$ is reminiscent of the $\langle g \rangle = 2.025$ resonance observed in benzonitrile solutions of $[CpCr(CO)_3]_2$ and originally assigned to $CpCr(CO)_3$.[10] This assignment was rejected by Morton and co-workers;[12b] the resonance is now believed to be due to a PhCN substitution product. The reaction with benzonitrile apparently goes to completion, and the $\langle g \rangle = 2.025$ resonance has a corresponding frozen-solution spectrum.[43] The resonances of types 3, 4, and 5 are very weak and do not correspond to any detectable features in the frozen-solution spectrum. Nonetheless, the type 3, 4, and 5 features are most likely due to reaction with adventitious traces of various nucleophiles in the sample preparations.

Summary. The compounds $[Na(diglyme)_{3/2}][(C_5Ph_5)Cr(CO)_3]$, $[PPN][(C_5Ph_5)Cr(CO)_3)]$, and $(C_5Ph_5)Cr(CO)_3$ have been prepared and characterized. The latter two complexes have spectroscopic and crystallographic properties similar to the analogous C_5H_5 and C_5Me_5 compounds. The 17-electron radical $(C_5Ph_5)Cr(CO)_3$ is thermally stable. ESR measurements suggest that in frozen solutions $(C_5Ph_5)Cr(CO)_3$ exists in two conformations with $^2A'$ and $^2A''$ ground states differing in energy by only 1–2 kJ/mol. The oxidized and reduced forms of the complex $(C_5Ph_5)Cr(CO)_3{}^{0,-}$ constitute a redox pair with a quasireversible charge transfer, $E° = -0.69$ V vs Fc in CH_2Cl_2.

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Supplementary Material Available: For $[PPN][(C_5Ph_5)Cr(CO)_3]$ and $(C_5Ph_5)Cr(CO)_3$, anisotropic thermal parameters (Tables 1S and 2S) and hydrogen-atom coordinates (Tables 3S and 4S) and, for $[PPN][(C_5Ph_5)Cr(CO)_3]$, an ORTEP drawing (11 pages). Ordering information is given on any current masthead page.

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[43] Although no ^{14}N hyperfine structure is observed in the isotropic spectrum, such structure is detectable in the frozen-solution spectrum: Krusic, P. J. Private communication.