consistent with its d^0 electronic configuration. The dioxo moiety gave rise to two bands in the IR spectrum, a strong one (ν_{sym}) at 914 cm^{-1} and a weaker shoulder (ν_{asym}) at 951 cm^{-1}.

Final proof of the structure was obtained by X-ray crystallography; the result is shown in Figure 1.[7] **2** is a monomeric half-sandwich and possesses a crystallographic mirror plane. Although the pentamethylcyclopentadienyl ligand is clearly η^5-bonded, its endocyclic C–C bonds show some bond length alternation toward a localized diene, and the Cr–C distances range from 2.19 to 2.37 Å. This distortion toward an η^1 structure is probably a manifestation of the strong trans influence of the oxo ligand. The Cr–C_{methyl} bond (2.05 Å) is only slightly shorter than comparable bonds in chromium(III) derivatives (2.09 Å on average),[5a] and the two symmetry-equivalent Cr–O distances (1.61 Å) fall squarely within the range found for known chromium oxo complexes (1.51–1.65 Å).[8]

Reaction of **1** with 0.5 equiv of O_2 under similar reaction conditions produced a dark green solution. Evaporation of the solvent yielded a solid residue from which a light green compound could be sublimed (room temperature, ca. 10^{-4} Torr) in very low yield. The same compound is produced in higher yield (52%) by reaction of **1** with trimethylamine *N*-oxide (Scheme I). Spectroscopic and analytical data of this compound were consistent with the formula $Cp^*Cr^V(O)(CH_3)_2$ (**3**).[9] In particular, the compound exhibited one strong band ($\nu_{Cr=O}$ 976 cm^{-1}) in the IR spectrum, which was shifted to 935 cm^{-1} upon use of $^{18}O_2$ in the synthesis. The magnetic susceptibility of **3** was measured in the temperature interval 4–290 K using a Faraday balance. The complex is paramagnetic, and the data were fitted with a Curie–Weiss expression.[10] The effective magnetic moment (corrected for diamagnetism, no detectable TIP) of **3** at 285 K is 1.76 μ_B, consistent with the d^1 configuration of pentavalent chromium.

The result of an X-ray structure determination of **3** is depicted in Figure 2.[11] The crystal contains two independent—albeit chemically equivalent—molecules in the asymmetric unit; they do not contain any crystallographically imposed symmetry elements. By comparison with **2**, the Cp* ligands of **3** exhibit no significant C–C bond length alternation, and the Cr–C_{ring} distances span a slightly smaller range. The average of the four Cr–C_{methyl} distances (2.043 (6) Å) does not differ significantly from that of **2**, while the Cr–O bonds of **3** are slightly shorter (average of 1.580 (3) Å).

Mixing equal amounts of **1** and **3** led to the formation of a dark green compound accompanied by liberation of pyridine (detected by ^{1}H NMR spectroscopy). On the basis of the spectroscopic data, we tentatively assign the structure $[Cp^*Cr^{IV}(CH_3)_2]_2(\mu_2\text{-}O)$ (**4**) to this paramagnetic complex.[12] Considering the great oxidizing power of chromium in its highest oxidation states, the considerable stability of the complexes described above is remarkable. C_6D_6 solutions of **2** decompose only slowly at room temperature ($t_{1/2}$ ca. 10 days), yielding mostly diamagnetic $[Cp^*Cr^V(O)(CH_3)]_2(\mu_2\text{-}O)$ (**5**).[13] The same compound is produced in a rapid reaction of **2** with triphenylphosphine. Chromium-based catalysts are used for the polymerization of small olefins;[14] however, neither **2** nor **3** showed any reaction with ethylene at room temperature and ambient pressure. The metal–carbon bond of **2** is not cleaved by methanol, indicating the highly covalent nature of the bond.

These results underscore the emerging notion that strongly π-donating oxo ligands greatly stabilize organometallic compounds in unusually high formal oxidation states and render their metal–carbon bonds nonpolar. It is our belief that the complexes described herein are only the tip of an iceberg laden with fascinating high-valent organochromium compounds. We are currently exploring this possibility.

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Supplementary Material Available: Tables of X-ray structure determinations of $Cp^*Cr(O)_2CH_3$ and $Cp^*Cr(O)(CH_3)_2$, including crystal data, atomic coordinates, anisotropic thermal parameters, and bond distances and angles (16 pages). Ordering information is given on any current masthead page.

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(7) Crystal data for **2**: $C_{11}H_{18}CrO_2$, orthorhombic, *Pnma*; $a = 12.6097$ (23), $b = 12.6518$ (26), $c = 7.4018$ (13) Å; $V = 1180.9$ (3) Å^3, $Z = 4$; $R(F) = 3.77\%$. Despite the similarity in *a* and *b*, photographic and diffraction experiments determined that the highest symmetry was orthorhombic. Two octants of data (2360 reflections, max $2\theta = 50°$) were merged, yielding 913 observed ($4\sigma F_o$) data. All non-hydrogen atoms were refined anisotropically, and hydrogen positions were included as idealized contributions.

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(9) **3**: ^{1}H NMR (C_6D_6) δ 4.9 (br); IR (KBr) 2967 (s), 2901 (s), 1431 (m), 1379 (m), 1134 (m), 1105 (m), 1024 (w), 976 (s), 802 (w), 513 (m); UV–vis (THF) 773 nm (ϵ 40), 328 (1350), 236 (3240); MS (70 eV) 233 (M^+, 2), 218 (19), 203 (94), 185 (100); mp 48 °C. Anal. Calcd for $C_{12}H_{21}CrO$: C, 61.78; H, 9.07. Found: C, 61.92; H, 9.23. Preliminary ESR studies (X-band) of **3** showed a septet (due to hyperfine coupling to the six equivalent methyl protons with $g = 2.000\,347$ and $a(^1H) = 6.3$ G).

(10) The susceptibility data was fitted with a Curie–Weiss expression ($\chi_m = [C/(T - \theta)] + \text{TIP}$). $C = 0.398$, $\theta = -3.3$ K, TIP $= -7.3 \times 10^{-5}$ emu.

(11) Crystal data for **3**: $C_{12}H_{21}CrO$, monoclinic, $P2_1/c$; $a = 14.438$ (3), $b = 14.188$ (3), $c = 13.499$ (3) Å; $\beta = 114.97$ (2)°; $V = 2506.8$ (9) Å^3, $Z = 8$, $R(F) = 5.14\%$. Preliminary photographic and diffraction experiments, which were performed due to similarity in the values of *a* and *b*, eliminated symmetries higher than monoclinic. Two octants of data (4888 reflections, max $2\theta = 50°$) yielded 3278 observed ($3\sigma F_o$) data. All non-hydrogen atoms were refined anisotropically, and hydrogen positions were included as idealized contributions.

(12) **4**: ^{1}H NMR (C_6D_6) δ −14.1 (br s, Cp*); IR (KBr) 2947 (s), 2907 (s), 2880 (s), 1487 (w) 1425 (m), 1377 (s), 1107 (m), 1020 (m), 978 (w), 937 (m), 804 (w), 696 (w) 502 (m); mp 97–99 °C.

(13) **5**: ^{1}H NMR (C_6D_6) δ 1.79 (s, 15 H), 1.21 (s, 3 H); IR (KBr) 2986 (m), 2911 (s), 1435 (m), 1377 (s), 1161 (w), 1109 (m), 1020 (m), 937 (s), 826 (s), 819 (w) cm^{-1}; MS (70 eV) 452 (M^+, 6), 288 (47), 134 (79), 119 (100). Anal. Calcd for $C_{22}H_{36}Cr_2O_3$: C, 58.39; H, 8.02. Found: C, 57.48; H, 7.53. The crystal structure of **5** has been determined and will be reported in a full paper.

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Biradical Character of a Closed-Shell Heteroaromatic Quinone

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There are so far very few definitive demonstrations of biradical contribution to the ground state of individual closed-shell organic molecules.[1] Tschitschibabin's hydrocarbon (**1**)[2] is one example, although opinions differ as to whether the compound exists as a singlet, a triplet, or a mixture of the two spin states.[3–25] The

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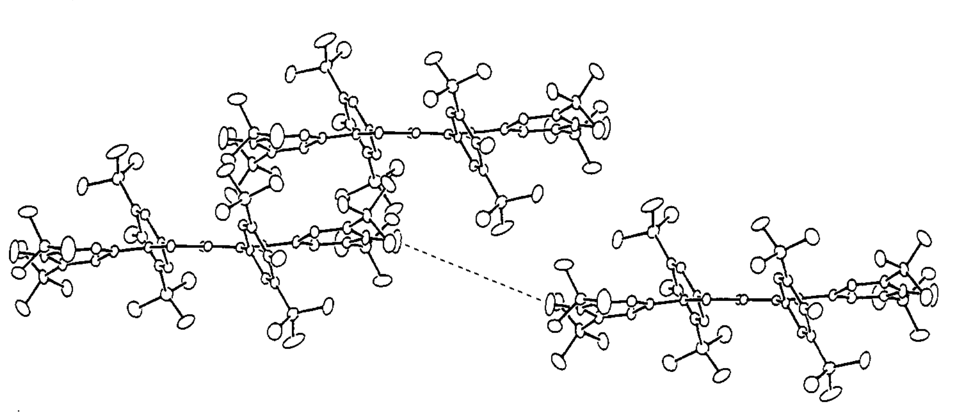
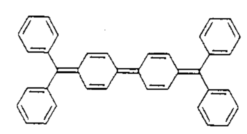
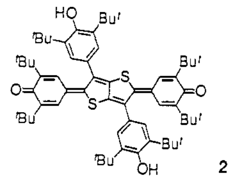


Figure 1. Packing of the molecules of **2** in the crystal structure, showing the two different contacts between the neighboring molecules.

problem seemed to be settled by Brauer et al., who succeeded in observing the triplet resonance signals in the ESR spectrum of polycrystalline **1**.[18-22] Recently, single crystals were obtained, and the sample afforded only a doublet ESR spectrum, like all previous ESR studies of **1**.[25] A clear-cut explanation cannot be offered for these conflicting observations, which are largely caused by the possibility of occluding paramagnetic impurities because of the high reactivity of **1** toward oxygen. Rather, the ESR study on other molecules with a comparable electronic structure to **1** provides an opportunity for solving this long-standing problem. We have now found that 2,5-dihydro-2,5-bis(3,5-di-*tert*-butyl-4-oxocyclohexadienylidene)-3,6-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)thieno[3,2-*b*]thiophene (**2**) is furnished with all characteristics of **1**.



1



2

As already reported, **2** was prepared in quantitative yield by the reaction of 2,3,5,6-tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)thieno[3,2-*b*]thiophene with an excess of iodine in the presence of triethylamine.[26] This quinone is intensely blue-colored (λ_{max} 634 nm, log ε 4.71) and stable in air for long periods of time. The single crystals suitable for X-ray structure analysis were obtained by recrystallization from benzene/methanol.[27] Figure 1 shows the packing with two different contacts between the neighboring molecules. Each molecule has a crystallographic center of symmetry on the midpoint of the central bond in the thienothiophene moiety. The thienothiophene moiety is planar with a maximum deviation of 0.03 Å. The oxocyclohexadienylidene group is approximately coplanar with the thienothiophene moiety, the dihedral angle between them being 13.1°. The hydroxyphenyl group has a large dihedral angle of 64.3° in relation to the thienothiophene. The intramolecular and shortest intermolecular distances between oxo atoms are 15.54 and 7.29 Å, respectively.

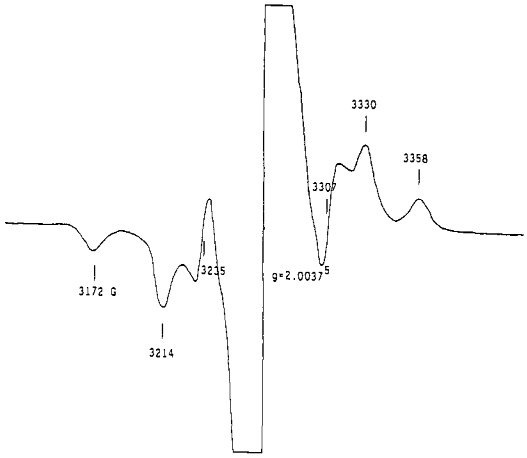


Figure 2. ESR spectrum of the single microcrystalline sample of **2** measured at 293 K.

The ESR spectrum of the single microcrystalline sample was measured at 293 K (Figure 2). Triplet resonance signals[28] are observable on the wings of the strong doublet signal at g = 2.003 75. The zero-field splitting constants, $|D'|$ and $|E'|$, defining the fine structure of the triplet, are 93 and 7.4 G, respectively,

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(27) Crystal data of **2**: $C_{62}H_{82}O_4S_2$, M_r 955.5; triclinic, $P\bar{1}$; a = 9.972 (2), b = 17.128 (4), c = 10.105 (3) Å; α = 114.14 (2), β = 94.59 (3), γ = 109.93 (2)°; V = 1431.3 (8) Å^3, D_x = 1.106 g cm^{-3}, Z = 1. Diffraction intensities were measured on a Rigaku four-circle diffractometer by using nickel-filtered Cu Kα radiation. During the intensity measurement, no decay was observed for three monitor reflections. A total 3737 reflections were collected up to 2θ = 110°, among which 3313 were observed reflections [$|F_o| > 3\sigma(F_o)$]. The crystal structure was solved by the direct method (SHELXS-86) (Sheldrick, G. M. *SHELXS-86*: *Crystallographic Computing 3*; Sheldrick, G. M., Krüger, C., Goddard, R., Eds.; Oxford University Press: Oxford, 1985; pp 175–189). The refinement of the crystal structure was proceeded by full-matrix least-squares (XRAY-76) (Stewart, J. M. XRAY-76: Report TR-446, University of Maryland, MD, 1976). All of the non-hydrogen atoms were refined by using anisotropic thermal parameters, while hydrogen atoms were located on the difference Fourier maps and refined isotropically. The final R index is 0.099.

(28) The half-field resonance ($\Delta m_s = \pm 2$) signal, the other indication specifying a triplet, was not observed in the temperature range measured.

and comparable, albeit slightly smaller, to those of **1** ($|D| = 144$ and $|E| = 5.0$ G). Furthermore, the spectrum measured at 100 K shows the fine structure also in the central signal. The $|D|$ value is ca. 5 G.[29] The intensity of the triplet signals gradually decreases if the temperature is lowered from 293 to 50 K, obviously implying that the triplet state is thermally accessible. The temperature dependence of the signal intensity obeys an equation of $I = N_b\mu_B{}^2g^2[1(1+1)][3kT\{1 + {}^1/_3\exp(\Delta E/kT)\}]$, where I is the triplet signal intensity, N_b the amount of biradical, μ_B the Bohr magneton, k the Boltzmann constant, and ΔE the energy gap between the singlet and the higher triplet. ΔE was estimated to be ca. 1.3 kcal/mol. On the other hand, the intensity of the central signal increased with lowering the temperature from 293 to 130 K and then reversely decreased in the temperature range lower than 130 K. According to an equation relating the signal intensity with temperature for a thermally-accessible triplet contaminated with an impurity monoradical, $I = N_m\mu_B{}^2g^2[{}^1/_2(1 + {}^1/_2)/3kT] + N_b\mu_B{}^2g^2[1(1+1)]/[3kT\{1 + {}^1/_3\exp(\Delta E/kT)\}]$ (N_m, monoradical amount), and by counting the exact spin amount of the signal with a reference TANOL, both N_b and ΔE were determined to be 3.9×10^{20} molecules/mol and ca. 0.5 kcal/mol, respectively. This thermally-accessible triplet has a smaller ΔE value compared with that of the triplet first described, suggesting a weaker spin–spin interaction. The observed N_b value indicates an unusually large biradical contribution of 0.07% to the ground state of **2**.[30] This molecule is unique as a closed-shell system. Indeed, two different spin–spin interactions occur in the single microcrystallines of **2**: one is the strong interaction with $\Delta E =$ ca. 1.3 kcal/mol, $|D| = 93$, and $|E| = 7.4$ G, and the other one is comparatively weaker ($\Delta E =$ ca. 0.5 kcal/mol and $|D| =$ ca. 5 G). It is concluded that the interactions are inter- and intramolecular, respectively, in view of the observation of only the $|D| =$ ca. 5 G triplet resonance signals in a polycrystalline sample of **2**, which is obtained by recrystallization from $CHCl_3$/*n*-hexane. In order to support this conclusion, the distance (R) between the two spins in interaction was roughly calculated from the observed $|D|$ value by using a point-dipole approximation, $R = \{{}^3/_2(g\mu_B/|D|)\}^{1/3}$ and comparing with that obtained by the X-ray structure analysis. The R values corresponding to $|D| = 93$ and ca. 5 G, are 6.7 and ca. 17.7 Å, respectively. The calculated values are consistent with the adjacent O–O distance (7.29 Å) between the two neighboring molecules and with the long-axis distance (15.54 Å) in the molecule, respectively.

The experimental evidence presented here is apropos to the interpretation of the ESR results of **1**. Since **1** has almost the same long-axis distance as **2**, the fine structure due to the interaction between the two spins residing in the molecule should be hidden under the strong monoradical signal of the impurity. Consequently, the triplet resonance signals with a splitting of 288 G can be considered to be caused by the spin–spin interaction between the two neighboring molecules of **1**. The fact that the signals appeared in the polycrystalline sample, but not in single crystals (contrary to **2**), reflects the necessity of molecular stacking to make significant intermolecular spin–spin interactions.

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Registry No. 1, 3624-94-0; **2**, 117474-91-6.

Supplementary Material Available: ORTEP drawing and full tables of fractional atomic coordinates and interatomic bond distances in **2** (4 pages). Ordering information is given on any current masthead page.

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[29] The $|E|$ value could not be determined because of overlap between the triplet resonance signals and the impurity monoradical signal.

[30] The degree of biradical contribution to the ground state is unusually large, considering that the biradical is in an electronically-excited singlet state and its thermally-accessible triplet state lies ca. 0.5 kcal/mol above.

Peptide Nucleic Acids (PNA). Oligonucleotide Analogues with an Achiral Peptide Backbone[1]

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Oligonucleotides that specifically recognize messenger RNA[2-6] or double-stranded DNA present unique opportunities for inhibiting protein synthesis (the antisense approach) or for modulating gene expression, e.g., via triple helix formation.[7,8]

The deoxyribose phosphate backbone of DNA has been modified in a number of ways to increase nuclease stability and cell membrane permeability, assuming that major changes would be deleterious to the "DNA hybridization properties". Consequently, derivatives such as mono-[9,10] or dithiophosphates,[11] methyl phosphonates,[12] borano phosphates,[13] etc.,[4] as well as formacetal,[14] carbamate,[15,16] and siloxane,[17] or dimethylenethio-, -sulfoxido-, and -sulfono-linked[18,19] species were prepared.

The synthesis of peptides is more versatile than oligonucleotide synthesis, allowing the facile design of an achiral backbone and relatively large-scale production. We therefore designed peptide nucleic acids (PNA), i.e., molecules where the individual nucleobases were linked to an achiral peptide backbone.

A suitable distance between nucleobases was estimated by detaching the backbone of one strand in a B-DNA duplex in a computer model and replacing it with amino acid units. The optimal number of bonds between the nucleobases was found to be six, which corresponds to that found in DNA (**1**, Scheme I), and the optimal number of bonds between the backbone and nucleobase to be two to three. This indicated that a backbone

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(1) Abbreviations and symbols used (standard oligopeptide nomenclature is used): H-, deprotected terminal amino group; $-NH_2$, C-terminal amido group; aeg, (2-aminoethyl)glycine; DMF, *N*,*N*-dimethylformamide; Boc, *tert*-butoxycarbonyl; Pfp, pentafluorophenyl.

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