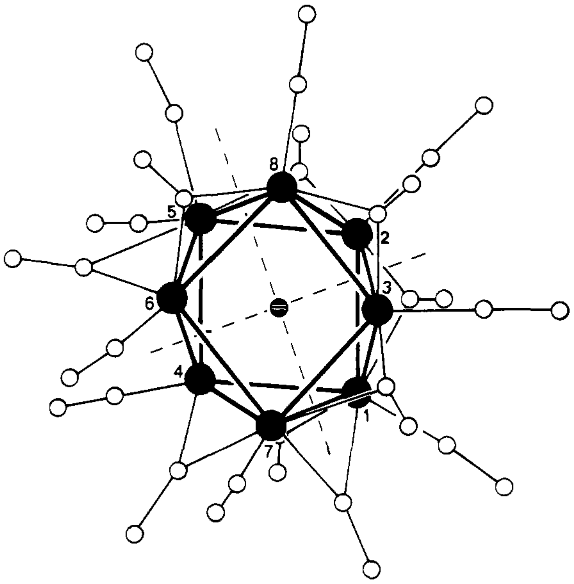

Figure 2. Structure of the $[Co_8(CO)_{18}C]^{2-}$ dianion. The twofold axes apply only to the metal atoms cluster and are indicated by dotted lines: one bisects Co_5–Co_8 and Co_1–Co_7, the other Co_2–Co_3 and Co_4–Co_6. The third axis is normal to the paper.

distortion, it is not equidistant from the cobalt atoms, the Co–C carbide distances being in the range 1.95–2.20 (2) Å with a mean value of 2.07 Å. The deformation of the antiprism and the long $Co–C_{carbide}$ distances probably represent a compromise situation in which bonding of the carbide atom is still possible in the large cavity of this polyhedron. The carbonyl groups can be divided into two sets of nine terminal and nine edge-bridging, although some of the bridging groups are markedly asymmetric. It is worth noting that the isoelectronic $Rh_8(CO)_{19}C$ has a different structure in which a trigonal prism of rhodium atoms has been capped both along a square face and along one of the triangular edges.[1]

The series of anions $[Co_6(CO)_{15}C]^{2-}$, $[Co_6(CO)_{14}C]^-$, and $[Co_8(CO)_{18}C]^{2-}$ provides a further example of the unusual stability of carbide carbonyl clusters,[1] which we attribute to the presence of additional bonds with the central carbon atom.

Further details of this and other studies of cobalt and rhodium[11] carbonyl carbide clusters will be reported later.

Acknowledgments. We thank the CNR for financial support and Nato for a grant.

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(6) The reaction has a considerable induction period (1–2 h), which can be eliminated by addition of preformed $Co_3(CO)_9CCl$.

(7) In acetone containing 3% benzene. D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

(8) The salt $[NMe_4][Co_6(CO)_{14}C]$ crystallizes in the $P\bar{1}$ space group with cell constants $a = 12.17$ (1) Å, $b = 13.28$ (1) Å, $c = 8.67$ (1) Å, $\alpha = 97.78$ (9)°, $\beta = 89.93$ (9)°, $\gamma = 98.23$ (9)°, and $Z = 2$. The structure has been solved using 1474 diffraction intensities collected by counter methods. The refinement is in progress, the current R value being 7.6%.

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(10) The salt $[NMe_3CH_2Ph]_2[Co_6(CO)_{18}C]$ crystallizes in the $P\bar{1}$ space group with cell constants $a = 19.02$ (2) Å, $b = 10.37$ (1) Å, $c = 12.81$ (1) Å, $\alpha = 116.43$ (9)°, $\beta = 88.90$ (9)°, $\gamma = 95.53$ (9)°, and $Z = 2$. The structure has been solved using 3560 diffraction intensities collected by counter methods. The refinement is in progress, the present conventional value of R being 8.9%.

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Chromium(II) Porphyrins and an Irreversible Dioxygen Complex

Sir:

We have recently been interested in the discovery of clean, high yield synthetic routes to low valent metalloporphyrins and more particularly in the generation of coordinatively unsaturated metalloporphyrins which are precursors to dioxygen complexes. The reaction of $Cr(acac)_2$[1] with $M^{III}Cl$(porphyrin) complexes, presumably occurring via a bridged chlorine transfer redox mechanism,[2] has proved to be a key step en route to dioxygen complexes derived from Fe(II)[3] and Mn(II)[4] species. We now report that this and another method can be exploited to reduce Cr(III) porphyrins and present evidence that distinguishes the Cr(II) d^4 formulation of the reduced products from the possible alternative, namely, a Cr(III) radical anion derived from porphyrin ring reduction. We also report the first example of a dioxygen complex derived from Cr(II).

Under scrupulously oxygen-free conditions, green CrCl(TPP)[5] is reduced by $Cr(acac)_2$ in toluene or THF to give red-brown solutions from which purple crystals of Cr(TPP) can be isolated.[7] Magnetic susceptibility measurements (Faraday method at 25 °C under an argon atmosphere) on these crystals and on the related Cr(OEP) are consistent with a high-spin d^4 configuration ($\mu_{eff}{}^{corr} = 4.8\ \mu_B$). The $M^{III/II}$ reduction potential for Cr is expected to be considerably more negative[8] than those of Co, Fe, and Mn raising the possibility of porphyrin ring reduction in preference to metal reduction. One criterion for distinguishing between metal and ligand redox reactions in metalloporphyrins, which apparently has wide generality,[9] is that the numerical difference between the half-wave potential of the first ligand oxidation in nitrile solvents and the first ligand reduction in Me_2SO, $\Delta E_{1/2}{}^{ox/red}$, is 2.25 ± 0.15 V. As with Cr(OH)(OEP),[10] cyclic voltammetry at Pt on CrCl(TPP) in benzonitrile and in Me_2SO (Figure 1) reveals six half-wave potentials relative to SCE. We have assigned these potentials as follows: +1.15 and −1.23 V to the first ligand oxidation and reduction, respectively; −0.86 V to $Cr^{III/II}$; +0.95 V tentatively to $Cr^{III/IV}$; +1.41 V to the second ligand oxidation; and −1.70 V to the second ligand reduction. We note that $\Delta E_{1/2}{}^{ox/red}$ is 2.38 V, and moreover, the differences between the first and second ligand reductions (0.47 V) and the first and second ligand oxidations (0.26 V) both lie in the normal ranges, 0.49 ± 0.08 and 0.29 ± 0.05 V, respectively.[11,12] Exhaustive coulometry at −1.0 V consumed one

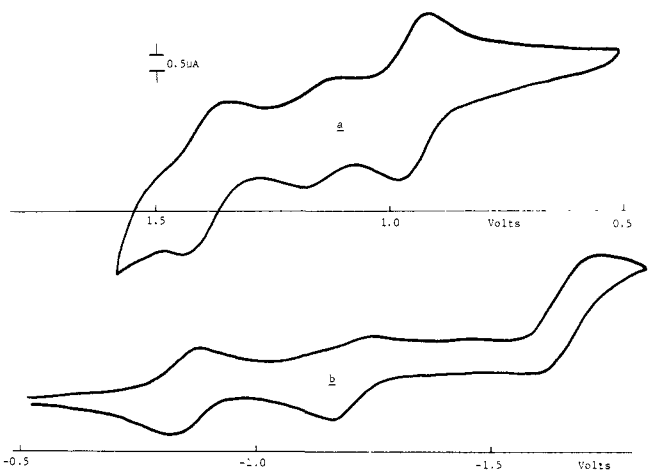


Figure 1. Cyclic voltammetry (0.2 V s^{-1}) referenced to SCE for CrCl(TPP): curve a shows oxidation in benzonitrile, curve b shows reduction in Me$_2$SO.

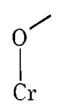
electron per molecule of CrCl(TPP) and the reduction product was identical in its visible spectrum to a chemically synthesized sample of Cr(TPP). Several features of the visible absorption spectra[13] of Cr(TPP) and Cr(OEP) in toluene or THF are also indicative of Cr(II) rather than Cr^{III}(TPP·$^-$). Upon reduction of Cr^{III}Cl(porphyrin) the Soret band undergoes a blue shift, gains intensity and decreases its half-width. Relevant comparison can be made with one of the few characterized porphyrin radical anions, Zn(TPP·)$^-$, where[14] the Soret band becomes broader, less intense, and undergoes a large *red* shift.[15] Moreover, our complexes show an absence of strong maxima around 800 nm, which if present are considered as indicators of radical anions.[16]

Nitrogen donor ligands (L) such as imidazole or pyridine, but not CO, add to Cr(TPP) giving rise to greenish solutions from which purple *five*-coordinate crystalline adducts Cr(TPP)L can be isolated. Cr(TPP)(py) can also be conveniently prepared in high yield by activated Zn treatment[17] of CrCl(TPP) in a THF/py/H$_2$O solvent mixture. Magnetic measurements on crystalline derivatives ($\mu_{\mathrm{eff}}^{\mathrm{corr}}$ = 2.8–2.9 μ_B) suggest a d^4 intermediate-spin configuration with two unpaired electrons consistent with axial ligation raising the energy of the d$_{z^2}$ orbital relative to its position in high spin Cr(TPP). Redox and spectral criteria similar to those discussed above also confirm the Cr(II) formulation although we note that particularly in the case of Cr(TPP)(NMeIm) the Soret band is markedly split (543, 423 nm) in a manner reminiscent of the formally isoelectronic d^4 Mn(III) porphyrins.[18] The explanation of this phenomenon apparently lies in the strong interactions between metal d and porphyrin π orbitals. An alternative view where the metal vs. ligand reduction crossover point[19] is approached seems to be discounted inasmuch as the Cr$^{III/II}$ and first ligand reduction half-wave reduction potentials are separated by greater than 0.5 V.

Although the possibility cannot presently be ruled out, we consider six-coordinate dimers [Cr(TPP)L]$_2$ unlikely. The occurrence of five-, rather than six-coordination in the adducts Cr(TPP)L is somewhat surprising inasmuch as the preference for *five*-coordination in transition metal M(TPP)L complexes has so far been restricted to those metals with singly occupied d$_{z^2}$ and/or d$_{x^2-y^2}$ orbitals.[4,20] However, chromium(II) suffers less atomic radius contraction than its higher atomic number neighbors, it is subject to a Jahn–Teller distortion, and it is possible that the well-documented[21] but poorly understood tendency of porphyrin ligands to kinetically labilize axial ligand binding sites may be manifest here as a thermodynamic effect.[25]

Of the scant literature reports[22,23] on synthetic Cr(II) porphyrins, our results corroborate the existence of Cr^{II} (*meso*-porphyrin IX dimethyl ester)[22] and suggest axial ligation may be responsible for the observed magnetic moment (2.84 μ_B). On the other hand, the visible spectral data and experimental details regarding the purported[23] Cr(TPP)·4H$_2$O imply that its characterization is less than definitive.

The very negative Cr(III/II) reduction potentials reflect the great desire of these chromium(II) complexes to become oxidized so that rapid aerobic oxidation of all compounds in solution to give Cr(III) products is not unexpected. The rate of oxidation can be slowed by cooling to −85 °C or by having high axial ligand concentrations, but we find no evidence for reversible oxygenation. Moreover, the crystalline solids are similarly oxygen sensitive except Cr(TPP)(py) which forms a unique dioxygen species answering to the properties of Cr(O$_2$) (TPP)(py). Ground crystalline Cr(TPP)(py) exposed to an oxygen atmosphere (500 torr for 16 h) takes up oxygen nearly stoichiometrically and manometric measurements reveal a Cr:O$_2$ ratio of 1:0.92 ± 0.05. A medium intensity infrared band which appears at 1142 cm^{-1} is assigned to ν(O–O). This band is absent in the isotopic ^{18}O$_2$ product and a very strong porphyrin band apparently masks the calculated harmonic oscillator shifted frequency at 1075 cm^{-1}. The close similarity of ν(O–O) with those observed for dioxygen complexes derived from electronically related Co(II) (e.g., 1123 cm^{-1} in (Co(O$_2$)(acacen)(py)))[24] strongly suggests a bent end-bound dioxygen moiety



and a Cr(III) superoxide formulation. The irreversibility of oxygen uptake and the changes in the visible spectrum are entirely consistent with this formulation. The magnetic moment (μ = 2.7 μ_B) indicates two unpaired electrons, and suggests that, formally speaking, one of the three t$_{2g}$ electrons on chromium is coupled with the odd electron on the superoxide ion. It is tempting to rationalize the diamagnetism of oxyhemoglobin in an analogous manner, namely, a low spin Fe(III) superoxide formulation with coupled spins.

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References and Notes

(1) Abbreviations used in this paper: acac = monoanion of acetylacetone; TPP = dianion of tetraphenylporphyrin; OEP = dianion of octaethylporphyrin; THF = tetrahydrofuran; Me$_2$SO = dimethyl sulfoxide; SCE = saturated calomel electrode; py = pyridine; NMeIm = *N*-methylimidazole.

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(13) λ_{max} in nm in THF (log ϵ): CrCl(TPP) 629 (3.7), 601 (3.9), 561 (4.0), 520 (3.6), 446 (5.2), 394 (4.5); Cr(TPP) 655 (3.65), 601 (3.75), 516 (3.95), 460 sh (4.2), 421 (5.3), 402 sh (4.5); Cr(TPP)(py) 675 (4.1), 610 sh (3.8), 530 (4.1), 455 sh (4.3), 420 (5.0); Cr(TPP)(NMeIm) 775 (3.4), 682 (4.0), 620 br (3.8), 532 (3.9), 453 (4.8), 423 (4.7), 404 sh (4.5).

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(25) Noted Added in Proof. We now have evidence for six-coordination.

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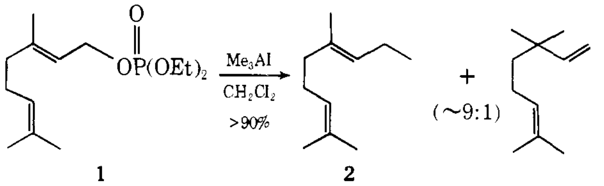
Novel Nonenzymic Heterolysis of an Allyl Phosphate Ester by Organoaluminum Reagents

Sir:

Although nonenzymic polyolefin terminal epoxide cyclizations are among the most fascinating biogenetic-like terpenoid syntheses and have received an immense amount of study,[1] another important counterpart of terpene biosynthesis, an allyl phosphate ester cyclization, has never been developed to a useful level due to the lack of a satisfactory reagent to promote the controlling heterolysis of these esters.[2] We now report the nonenzymic SN1-like heterolysis of the phosphate ester with concurrent regioselective generation of new C–S, C–N, C–O, and C–C bonds akin to that occurring in the biological process.[3]

Reaction of geranyl diethyl phosphate (**1**)[4] with trimethylaluminum (4.0 equiv) in methylene chloride under argon at −78° for 30 min, 0° for 1 h, and 20° for 2.5 h led to efficient (>90%) cross coupling in a stereospecific manner; none of the *Z*-isomer of **2** was present in the crude reaction mixture by GLC analysis.[5] A dramatic alteration in the course of the reaction occurred when the reaction of trimethylaluminum was conducted with neryl diethyl phosphate (**3**);[4] although limonene (**4**) and terpinolene (**5**) were formed with no trace of **2**, the predominant product (68%) was 4-*tert*-butyl-1-methylcyclohexene (**6a**), resulting either from a direct alkylation of nonclassical carbonium ion **7** or an alkylation of classical terpinyl ion **8** (or **9**).[2] The analogous alkylative cyclization using triethylaluminum or triisobutylaluminum in methylene chloride afforded **6b** or **6c** in 70 and 68% yields, respectively, starting from **3**. These striking observations demonstrate unequivocally that intermediary allylic carbonium ions (or equivalents) from **1** and **3** strictly preserve their steric integrities in the above transformations.[6]



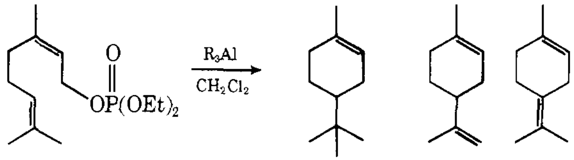
1 **2**

Table I.[a] Substitution of 1 and 3

$$RCH_2O\overset{\overset{\displaystyle O}{\|}}{P}(OEt)_2 \xrightarrow[\text{hexane}]{Me_2AlX\ (4\ \text{equiv})} RCH_2X$$

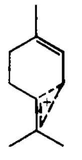
			Product	
Aluminum reagent (method of preparation)[b]	Substrate	Reaction conditions Time (h) Temp (°C)	X	Isolated yield[c] (%)
$Me_2AlS\text{-}t\text{-}Bu^7$ (A)	1	0.5, 0	S-*t*-Bu	97
$Me_2AlS\text{-}t\text{-}Bu^7$ (A)	3	0.5, 0	S-*t*-Bu	92
Me_2AlSPh^7 (A)	3	0.5, 0	SPh	83
$Me_2AlNHPh^8$ (B)	1	0.5, 0; 12, 20	NHPh	74
$Me_2AlNHPh^8$ (B)	3	0.5, 0; 12, 20	NHPh	82
Me_2AlOPh^9 (B)	1	0.3, 0; 1.5, 20	OPh	85
Me_2AlOPh^9 (B)	3	1, 0; 1, 20	OPh	77

[a] Most of these reactions were run on a 1 mmol scale. The yields are not necessarily optimum. [b] Method of preparation: A, prepared in situ by treatment of the corresponding thiol with trimethylaluminum (1.0 equiv) in hexane at 0°; B, prepared by the reported procedure and isolated by recrystallization. [c] Isolated by chromatography on silica gel and adequately characterized by analytical and spectral data.



3 **4** **5**

6a, R = Me
6b, R = Et
6c, R = *i*-Bu



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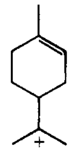

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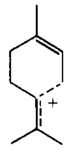

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In view of the efficiency of the mild and stereospecific heterolysis of allyl phosphate ester by trialkylaluminum reagents, the behavior of certain organoaluminum reagents of type R_2AlX (X = SR, NHR, or OR)[7-9] was studied. Treatment of geranyl or neryl phosphate ester in hexane with aluminum reagents (4 equiv) results in formation of substitution products *with regio- and stereospecific manner.* The examples cited in Table I illustrate the synthesis of sulfides, amines, and ethers using the indicated reactants and reaction conditions.

In contrast to the substitution of **3** by aluminum reagents in hexane (Table I) that gave only a small amount or (in most cases) none of the cyclic products, *the cyclic dienes predominated using methylene chloride as solvent.* Thus, treatment of the ester **3** with dimethylaluminum phenoxide in methylene chloride at 0° for 1 h and 20° for 3 h furnished limonene (**4**) and terpinolene (**5**) in 58 and 11% yields, respectively, contaminated by only 8–10% of neryl phenyl ether. Similarly, dimethylaluminum anilide gave rise to **4** and **5** in 49 and 13% yields, respectively. The pronounced solvent effect on the course of the reaction must be related in part to the nature of the ion pair in the transition state. In nonpolar solvent a tight ion pair might be involved, while in a more polar solvent system the ion pair might be more widely separated and the cyclization takes place rather easily.

For preparing the cyclized products even more selectively, we next examined the behavior of certain aluminum reagents of type $R_2AlXAlR_2$ (X = S, PhN, and O)[10] which may form