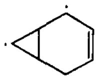
radicals dispose of a stabilization energy of several kilocalories per mole.[17] Furthermore an easy ring enlargement[12] as **14** → **15** is not available to **18**, the rearrangement of which should therefore be encumbered with more constraints.



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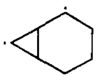

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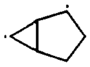

18

Another recent finding seems to support the intermediacy of diradicals in bicyclobutane rearrangements. Naphtho[1.8]tricyclo[4.1.0.0^{2,7}]heptene transforms to the corresponding *cis*-cyclobutene at temperatures[18] as low as those necessary to decompose **5.** In this case the benzyl type stabilization of one radical center in the intermediate would account for the easy reaction.

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Reaction of Oxygen with Dicyanotris(dimethylphenylphosphine)cobalt(II). Synthesis, Structure, and Reactivity of a Novel Cobalt–Dioxygen Adduct

Sir:

The reactions of O_2 with low-spin pentacoordinate cobalt(II) complexes are of widespread occurrence and characteristically follow the course of eq 1 to form either terminally bonded mononuclear or O_2-bridged binuclear adducts (types **1** and **2**, respectively).[1]

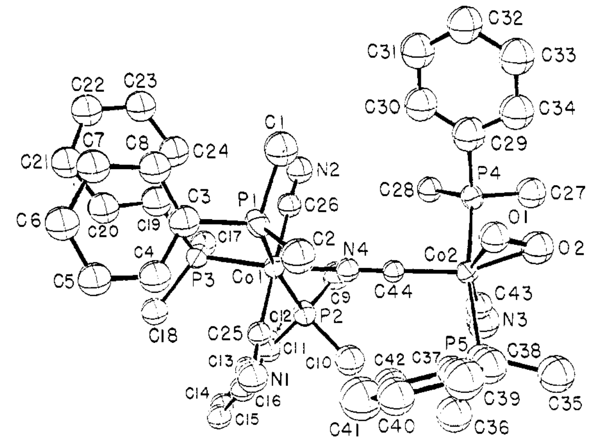

Figure 1. Molecular structure of $[Co_2(CN)_4(PMe_2Ph)_5(O_2)]$.

$$[L_5Co^{II}] \xrightarrow{O_2} \left[L_5Co{-}O{\diagup}O\right] \xrightarrow{L_5Co^{II}} \left[L_5Co{-}O{\diagup}O{-}CoL_5\right] \qquad (1)$$

1 2

While the bonding in such adducts is still a subject of active discussion (formulation as cobalt(III) complexes being generally favored) several complexes of each type have been structurally characterized and found to be in accord with the above representations.[1-6] Such structures have, accordingly, also been generally assumed for other cobalt(II)–O_2 adducts.[1] In view of this, our finding of a rather different, previously unrecognized, structure for the 1:2 adduct formed by reaction of O_2 with $[Co^{II}(CN)_2(PMe_2Ph)_3]$ (Me = CH_3, Ph = C_6H_5), which together with the characterization of this adduct are the subjects of this communication, represents a quite unexpected result. This finding also prompts reexamination of hitherto accepted assignments of the structures of certain other cobalt(II)–O_2 adducts.[7,8]

Passing a stream of O_2 through a benzene solution of $[Co(CN)_2(PMe_2Ph)_3]$ for about 8 hr resulted in formation of the adduct (**3**) in accord with the stoichiometry of eq 2. Addition of hexane resulted in precipitation of brown crystals of **3**: electronic spectrum of **3** (in methanol), λ_{max} 295 nm (ϵ 2.1 × 10^4 M^{-1} cm^{-1}); infrared (Nujol), ν_{CN}, 2085 and 2105 cm^{-1}, ν_{O_2}, 881 cm^{-1}.

$$2[Co(CN)_2(PMe_2Ph)_3] + O_2 \longrightarrow \underset{\textbf{3}}{[Co_2(CN)_4(PMe_2Ph)_5(O_2)]} + PMe_2Ph \qquad (2)$$

Crystals of $[Co_2(CN)_4(PMe_2Ph)_5(O_2)]\cdot\frac{1}{2}C_6H_6$, grown from benzene-acetone, belong to the *Fdd*2 space group with cell dimensions a = 33.583 (4), b = 30.471 (4), and c = 19.449 (2) Å and ρ_{obsd} = 1.317 and ρ_{calcd} = 1.313 g/cm^3 for 16 formula units per unit cell. Data were collected on a Picker FACS-I diffractometer, using Mo Kα radiation and a graphite monochromater. A total of 2212 independent reflections ($2\theta \leq 40°$, relative structure factors $>3\sigma_F$) were used in the solution and refinement of the structure. The structure was solved by direct methods using a modified version of MULTAN.[9] In the refinement by full-matrix least-squares methods, the benzene molecule and phenyl groups were treated as rigid bodies, the Co and P atoms were assigned anisotropic thermal parameters, and the other atoms were assigned isotropic thermal parameters. H atoms were included as fixed atom contributions assuming r_{C-H} = 0.95 Å and normal geometries (the orientation of the methyl groups being determined by a least-squares fit of the difference-Fourier at the final stages of refinement).

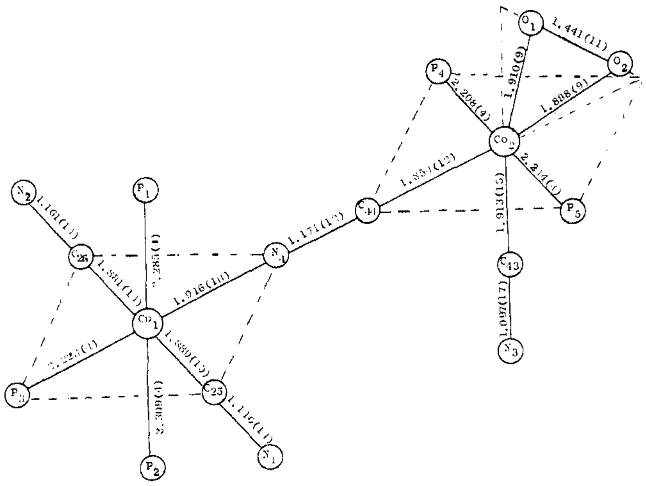

Figure 2. Representation of the inner coordination spheres of $[Co_2(CN)_4(PMe_2Ph)_5(O_2)]$. Selected bond angles (deg): O_1-Co_2-O_2, 44.6 (3); O_1-Co_2-P_5, 86.5 (3); O_2-Co_2-P_5, 89.4 (3); O_1-Co_2-P_4, 92.8 (3); O_2-Co_2-P_4, 82.2 (3); O_1-Co_2-C_{43}, 151.8 (5); O_2-Co_2-C_{43}, 107.8 (5); O_1-Co_2-C_{44}, 107.7 (5); O_2-Co_2-C_{44}, 151.2 (5); P_4-Co_2-P_5, 168.7 (2); P_4-Co_2-C_{43}, 87.7 (4); C_{43}-Co_2-C_{44}, 100.4 (6); Co_2-C_{44}-N_4, 177.0 (10); Co_1-N_4-C_{44}, 175.1 (9); P_1-Co_1-P_2, 166.3 (2); P_1-Co_1-P_3, 96.9 (2); P_1-Co_1-N_4, 84.9 (3); P_1-Co_1-C_{25}, 87.4 (4); P_1-Co_1-C_{26}, 92.7 (4); P_2-Co_1-P_3, 96.1 (2); P_3-Co_1-N_4, 173.0 (3); C_{25}-Co_1-C_{26}, 179.8 (5).

The final reliability factors were $R = 0.058$ and $R_w = 0.046$.[10]

The structure of **3** is depicted in Figures 1 and 2. The most striking feature, which distinguishes this complex from other known binuclear cobalt-dioxygen adducts cited earlier, is that the two Co atoms are bridged by a CN^- ion rather than by the O_2 molecule. The O_2 molecule, in turn, is coordinated to one of the Co atoms as a bidentate ligand in a manner that has hitherto proved characteristic of the O_2 adducts of d^8 (Ir^I, Rh^I, Co^I, Ru^0, Os^0) and d^{10} (Pt^0, Pd^0, Ni^0) complexes.[1] The O-O bond length of 1.44 Å in **3** is in the range of other known O-O bond lengths in adducts of the latter type, e.g., 1.30 Å in $[IrCl(CO)(PPh_3)_2(O_2)]$,[11] 1.51 Å in $[IrI(CO)(PPh_3)_2(O_2)]$,[12] 1.42 Å in $[Co(Ph_2PCH{=}CHPPh_2)_2(O_2)]^+$,[13] 1.42 Å in $[Rh(Ph_2PCH_2CH_2PPh_2)_2(O_2)]^+$,[14] etc. The nearly linear Co-N-C-Co arrangement also finds parallels in other CN-bridged binuclear cobalt complexes, for example, $[(NH_3)_5CoCNCo(CN)_5]$.[15] Other structural features of **3** are conventional. Apart from the distortions associated with the small O-Co-O angle (44.6°), the arrangements of ligands around each Co atom approximate idealized octahedra and there are no unusual bond lengths or angles.

Preliminary kinetic measurements on reaction 2 yielded a rate law of the form of eq 3 where $k_3 \approx 1 \times 10^{-4}\ M^{-1}\ \mathrm{sec}^{-1}$ in benzene at 25°.

$$-d[O_2]/dt = k_3[Co(CN)_2(PMe_2Ph)_3]^2[O_2][PMe_2Ph]^{-1} \tag{3}$$

This result, together with the unusual structure of **3**, can be accommodated by the following mechanism for reaction 2, according to which $k_3 = K_4k_5$.

$$[Co^{II}(CN)_2(PMe_2Ph)_3] + O_2 \overset{K_4}{\rightleftharpoons} [Co^{II}(CN)_2(PMe_2Ph)_2(O_2)] + PMe_2Ph \tag{4}$$

$$[Co^{II}(CN)_2(PMe_2Ph)_2(O_2)] + [Co^{II}(CN)_2(PMe_2Ph)_3] \xrightarrow{k_5} [(Me_2PhP)_3(NC)_2\underbrace{Co^{II}NC}_{e^-}\underbrace{Co^{II}(CN)(PMe_2Ph)_2(O_2)}_{2e^-}] \longrightarrow \mathbf{3} \tag{5}$$

According to this interpretation the binuclear complex **3** is formed through a CN-bridged inner sphere electron transfer reaction between $[Co^{II}(CN)_2(PMe_2Ph)_3]$ and the O_2-substituted complex, $[Co^{II}(CN)_2(PMe_2Ph)_2(O_2)]$. The driving force for this is reinforced by the ability of the O_2 ligand to remove electron density from the resulting "Co^I" center. The formal oxidation states of the final product **3**, accordingly, correspond to $[Co^{III}NCCo^{III}(O_2^{2-})]$, assignment of the +3 oxidation states to the two Co atoms being consistent with the substitution inertness of **3**.

The above mechanism and corresponding kinetic behavior (eq 3) are closely related to those previously reported[16] for the carbonylation of $[Co^{II}(CN)_5]^{3-}$. The similarities between the two systems reflect the effectiveness of CN^-, in each case, as an inner-sphere bridging ligand for electron transfer between two Co^{II} ions, while the differences emphasize the ability of the O_2 ligand (in a manner frequently ascribed to NO ligands[17] but not shared by CO) to accommodate highly varying degrees of electron transfer from a metal atom, with corresponding enhancement of the range of effective oxidation states accessible to the latter.

In methanol solution the adduct **3** reacted with added PMe_2Ph to form Me_2PhPO and regenerate $[Co(CN)_2(PMe_2Ph)_3]$ according to eq 6 with a rate-law approximating, $-d[\mathbf{3}]/dt = k_6[\mathbf{3}][PMe_2Ph]$, where $k_6 \approx 4 \times 10^{-5}\ M^{-1}\ \mathrm{sec}^{-1}$.

$$[Co_2(CN)_4(PMe_2Ph)_5(O_2)] + 3PMe_2Ph \longrightarrow 2[Co(CN)_2(PMe_2Ph)_3] + 2Me_2PhPO \tag{6}$$

Taken together, reactions 2 and 6 constitute a catalytic cycle for the oxidation of PMe_2Ph to Me_2PhPO by O_2 under the catalytic influence of $[Co(CN)_2(PMe_2Ph)_3]$. This behavior is similar to that reported previously for $Pt(PPh_3)_3$ which catalyzes the oxidation of PPh_3 to Ph_3PO through a mechanism involving the dioxygen adduct, $[Pt(PPh_3)_2(O_2)]$, as an intermediate.[18] In this context a significant feature of the present system is that the dioxygen adduct involved, i.e., **3**, is coordinatively saturated whereas prior examples of facile oxidation of such substrates have generally been associated with coordinatively unsaturated adducts such as $[Pt(PPh_3)_2(O_2)]$.[1] It has been suggested that coordinative unsaturation may facilitate such oxidation processes through mechanisms involving attack of the phosphine on the metal.[1,18] We are continuing to investigate the mechanisms of this and related catalytic oxidations.

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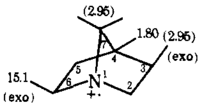
An Electron Spin Resonance Study of the Bridgehead Aminium Radicals Derived from 1-Azabicyclo[2.2.1]heptane, 1-Azabicyclo[2.2.2]octane, and 1-Azaadamantane[1]

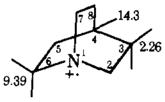
Sir:

The geometry and electronic configuration of transient chemical species have been the goal of numerous studies. Carbonium ions are known to prefer a planar geometry while unconjugated carbanions exist in a pyramidal configuration.[2] Carbon-centered free radicals are generally planar or nearly so.[2-4] However, out-of-plane deformation of a free radical is considerably easier than for a carbonium ion and many appropriately substituted or electronically compelled carbon-centered radicals have been shown to be nonplanar.[4] Krusic, Rettig, and Schleyer have recently concluded from ESR and INDO studies that the 1-adamantyl and 1-bicyclo[2.2.2]octyl radicals are pyramidal with the bridgehead carbon atoms about 0.4 Å out of a plane defined by the attached three carbons.[5] Mishra and Symons[6] have observed $a^{13C} = 136.7$ G for the central carbon in the 1-adamantyl radical which corresponds to 12% 2s character and supports a distinctly pyramidal configuration.

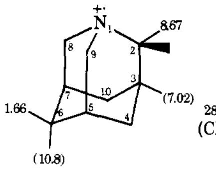
Many studies concerned with the stability and reactivity of free radicals and carbonium ions generated at the bridgehead positions of the bicyclo[2.2.1]heptyl, bicyclo[2.2.2]octyl, and adamantyl ring systems have been conducted.[2] We have demonstrated in previous studies[7] that dialkylaminium radicals, $R_2NH\cdot^{+}$, are planar about the nitrogen atom and we believed it would be of significance to investigate by ESR the corresponding bridgehead aminium radicals, **1–3**. On the basis of both Pauling's arguments[8] and INDO calculations,[9] it is expected that the out-of-plane bending force constant for an aminium radical should be intermediate between that of an alkyl radical and that of a carbonium ion. It follows that **2** and **3** should be less pyramidal as compared to the analogous carbon-centered radicals providing that the caged structures are sufficiently flexible to allow a flattening distortion about the bridgehead nitrogen atoms. The present results appear to support this conclusion.



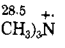
a^{N} = 30.2
1



25.1
2



21.6
3



$(CH_3)_3\overset{+\cdot}{N}$
20.7
4

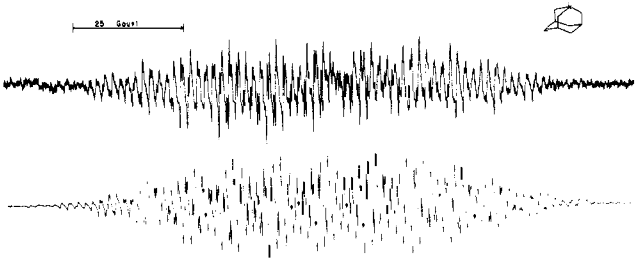


Figure 1. Experimental (above) and computer simulated (below) ESR spectra of the radical cation derived from 1-azaadamantane in CF_3SO_3H at −50°.

The radicals were generated by ultraviolet photolysis of the corresponding amine-Cl_2 adducts in CF_3SO_3H at 0 to −50°. The spectrum of **3** is shown in Figure 1 along with the simulated spectrum; hyperfine coupling constants in gauss are noted above for **1–4.**[10] Several features are worthy of note: (a) a^{N} increases in the order **4 < 3 < 2 < 1**; (b) the proton hyperfine interactions for **2** and **3** are considerably larger than in the corresponding bridgehead carbon-centered radicals studied by Krusic et al.;[5] (c) the large δ coupling in **2** (14.3 G, verified by deuterium labeling) does not have its counterpart in **1**.

On the basis of the ESR results and INDO calculations we conclude that the bridgehead radicals are pyramidal about the nitrogen atoms but that there is a trend toward planarity in going from **1** to **3**. Complete INDO geometry optimizations[11] for **1**, **2**, and **3** indicate that the nitrogen atom is external to a plane defined by the attached three carbon atoms by 0.44, 0.32, and 0.30 Å, respectively; the trimethylaminium radical is calculated to be planar. The calculated a^{N} values are less definitive at 20.4, 20.9, and 18.8 G for **1**, **2**, and **3**, respectively; a^{N} is calculated as 15.1 and 36.8 G for planar and tetrahedral (N is 0.49 Å out-of-plane of attached carbons) $(CH_3)_3N\cdot^{+}$, respectively. The observed a^{N} values are quite small in view of a predicted coupling of 550 G for unit spin density in a nitrogen 2s orbital[13] but, as attested to by the INDO results and localized orbital considerations,[9] are not inconsistent with pyramidal geometries about the nitrogen atoms in **1–3**.

The calculated values for a^{H} are in at least qualitative agreement with the experimental proton hyperfine coupling constants with the major trends reproduced. In particular, large values of a_{δ}^{H} for **2** and the axial protons in **3** are predicted as well as the low value of the δ hydrogen in **1**. The large a^{H} of the exo β hydrogens and negligible interaction with the endo β protons in **1** are verified. Interestingly, movement of the bridgehead nitrogen inward predicts a calculated *decrease* in a^{H} for H_4 in **2** but an *increase* for this proton in **1**. This supports other data[5] suggesting that a through-bond mechanism for spin delocalization[14] is operative in such bicyclic radicals and that a backlobe effect is probably unimportant. The small coupling to H_4 in **1** apparently results from a cancellation of the positive spin density on this proton induced via the C_2–C_3 and C_5–C_6 bonds by the negative spin density transmitted effectively through the shorter C_7 methylene bridge.

These and other aspects of these interesting bridgehead radicals will be discussed in the full publication of this work.

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