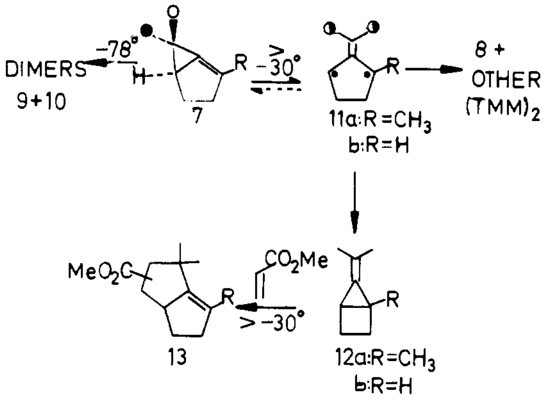
dimerizes without perturbation of the configuration at C_6. When unlabeled, compound **10** shows six three-proton singlets corresponding to methyl groups a-f. Two of the signals of **10**-d_6, examined in benzene-d_6, completely disappear leaving four undiminished CH_3 resonances. This finding, taken together with the observations on **8** (below), supports the previous conclusion[7] that products of the $[\sigma + \pi]$ cycloaddition mode do not involve a TMM intermediate.

However, compound **8** is formed with exactly 1.5 deuterium atoms in each of the allylic methyl groups a and b, as can be deduced from the signals at δ 1.79 and 1.69, each of which is just half as intense as the 6-proton singlet of the c Me groups at δ 1.22. Note that the [2 + 2] dimer **9** formed in the same reaction mixture at 0 °C still shows completely stereospecific labeling, as at −78 °C.

These observations may be explained by a mechanism in which **8** is formed from the TMM **11a** by the sequence **7** → **11a** → **8**. The TMM **11a** lives long enough as the singlet biradical to undergo complete stereorandomization by torsion about the exocyclic C-C bond,[2,9] but ring closure back to the bicyclo[3.1.0]hex-1-ene **7** is slow on the time scale of dimerization.

Ring closure of a TMM of type **3** to structure **1a** thus seems to be unfavorable, as is also suggested by the highly specific formation of 5-alkylidenebicyclo[2.1.0]pentanes (**2a**) in the photolysis of 7-alkylidene-2,3-diazanorbornenes,[1,2,10] presumably via a TMM intermediate. Another instance of this now appears in the apparently unidirectional thermal rearrangement of the bicyclo[3.1.0]hex-1-ene **7** to the 5-alkylidenebicyclo[2.1.0]pentane **12**. Metalation of **5a** (undeuterated) at −30 °C, cooling, and treatment with MeOH at −78 °C, storage for 8 min, addition of methyl acrylate, and warming to room temperature give not only dimers **9, 10,** and **8,** but also ~20% of a mixture of 1:1 cycloadducts of the familiar[11] type **13**. Apparently, **7,** which only dimerizes at −78 °C,[12] rearranges to **12a** at −30 °C. The latter compound, like its analogue **12b,**[1] can be stored but reacts with an olefinic trapping agent at higher temperature.[13]



The present results suggest that the transition state leading from **11a** to **7** must be substantially higher in energy than that leading to **12a**. It seems likely that this energy ordering may apply to the bicyclic molecules themselves. Hence, bicyclo[3.1.0]hex-1-enes (**1a**), like 5-alkylidenebicyclo[2.1.0]pentanes (**2a**), may contain a bond whose rupture to give the ground-state triplet TMM common to both bicyclic species is nearly thermoneutral if not actually exothermic.

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(8) Compound **10** shows NMR singlets at δ 1.69, 1.21, 1.19, 1.00, 0.78, and 0.71 (3 H each, CH_3) and a multiplet at δ 2.66–2.45 (3 H, allylic H). The mass spectrum shows a parent peak at *m/e* 244, corresponding to $C_{18}H_{28}$.
(9) Stereorandomization cannot be distinguished by this experiment from a stereospecific reaction involving an even number of olefinic torsions of the exocyclic double bond in one partner and an odd number in the other. We consider this an unlikely alternative.
(10) M. G. Lazzara, Ph.D. Dissertation, Yale University, planned for 1979, finds traces (1–3%) of adducts of **1a** type products in some instances.
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(12) In a control experiment, we find that metalation of **5a** at −78 °C instead of −30 °C, followed by the same treatment, gives no cycloadducts **13** but only the usual dimers **9** and **10** obtained in the absence of methyl acrylate.
(13) It is still not clear whether the cycloadditions of **12a** and **12b** with olefins occur directly or by preliminary formation of singlet diyls **11a** and **11b.**

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Synthesis and X-ray Characterization of the $[M_6N(\mu\text{-}CO)_9(CO)_6]^-$ (M = Co, Rh) Anions. A New Class of Metal Carbonyl Cluster Compounds Containing an Interstitial Nitrogen Atom

Sir:

We report here the first examples of carbonyl cluster compounds containing interstitial nitrogen: the $[M_6N(CO)_{15}]^-$ (M = Co, Rh) anions.

The reaction of $K_2[Co_6(CO)_{15}]$[1] in THF with $NOBF_4$[2] gives a mixture of Co(II), $Co(CO)_3NO$, traces of $Co_4(CO)_{12}$, and the new anion $[Co_6N(CO)_{15}]^-$ which is separated as the orange-red potassium salt (40-50% yield) by evaporation to dryness, dissolution in MeOH, and filtration from KBF_4, followed by precipitation with water and concentration in vacuo.

The similar reaction of $[Rh_6(CO)_{15}]^{2-}$ [3] with $NOBF_4$ gives only very low yields of the analogous rhodium compound (<10%).[4] However, better yields (40-60%) of $K[Rh_6N(CO)_{15}]$ have been obtained from the reaction of a methanolic solution of $K_3[Rh_7(CO)_{16}]$[3] with a 1:1 mixture of CO and NO followed by filtration, precipitation of the yellow potassium salt by addition of aqueous KCl (3%), concentration in vacuo, filtration, and washing the precipitate with water until the washings are colorless.

The potassium salts can be transformed into the $[(Ph_3P)_2N]^+$ (PPN^+) or Ph_4P^+ salts by metathesis in aqueous Pr^{i}OH.

The structure of $PPN[Co_6N(CO)_{15}]$[5] has been investigated

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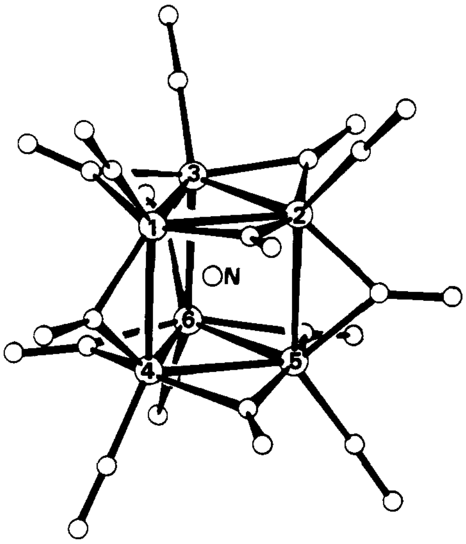

Figure 1. The structure of the anion $[Co_6N(CO)_{15}]^-$. The Co-Co bond lengths follow: Co(1)-Co(2), 2.515 (2); Co(1)-Co(3), 2.535 (2); Co(1)-Co(4), 2.561 (2); Co(2)-Co(3), 2.527 (2); Co(2)-Co(5), 2.559 (2); Co(3)-Co(6), 2.572 (2); Co(4)-Co(5), 2.506 (2); Co(4)-Co(6), 2.502 (2); and Co(5)-Co(6), 2.519 (2) Å.

by X-ray diffraction[6] and the structure of the anion, of idealized D_{3h} symmetry, is shown in Figure 1. It contains a trigonal prismatic cluster of metal atoms with the nitride ligand in the central cavity; the carbonyl stereochemistry is similar to that found in the isoelectronic carbido species $[M_6C(CO)_{15}]^{2-}$ (M = Co, Rh).[7,8] The Co-Co distances within the basal triangles (mean 2.517 Å) are shorter than the interbasal distances (mean 2.564 Å); the same difference has been observed previously in $[Rh_6C(CO)_{15}]^{2-}$. The Co-N bond lengths are all similar (range 1.925 (9)-1.957 (8) Å) with a mean value of 1.938 Å. The resulting covalent radius of the interstitial nitrogen atom, 0.67 Å, shows the expected decrease with respect to the experimental carbide radius in $[Rh_6C(CO)_{15}]^{2-}$ (0.74 Å). The Co-C and C-O distances for terminal, basal edge-bridging and interbasal edge-bridging groups have mean values of 1.71 and 1.16, 1.96 and 1.17, and 1.90 and 1.19 Å, respectively.

The nature of the interstitial atom has been unambiguously established by consideration of the following NMR and IR data.

(i) The ^{13}C NMR spectra of $[M_6N(CO)_{15}]^-$, prepared from ^{13}CO-enriched $[Co_6(CO)_{15}]^{2-}$ and $[Rh_7(CO)_{16}]^{3-}$, have *no* resonances in the carbide region (250-400 ppm)[9,10] and contain only resonances associated with the symmetrical distribution of 15 CO's[11] as shown in Figure 1; this excludes $[M_6C(CO)_{14}(NO)]^-$ as a possible formulation since this would not only require a carbide resonance but, because of the reduced symmetry, would require more carbonyl resonances.

(ii) In the ^{14}N NMR spectra, the resonances[12] are found to be well away from the region associated with known metal nitrosyl resonances (δ ±50 ppm, external reference CD_3NO_2) and in the rhodium case there is some evidence of resolution of this resonance. This resolution is fully realized in the ^{15}N NMR spectrum of the analogous ^{15}N-enriched rhodium compound which clearly shows five lines (Figure 2) with relative intensities appropriate for a septet[12] and the ratio of $^1J(Rh^{15}N)$ to $^1J(Rh^{13}C)$ (for the carbide resonance in $[Rh_6C(CO)_{15}]^{2-}$ [10]) is in good agreement with the ratio predicted from the known gyromagnetic ratios of ^{15}N and ^{13}C. The possibility that this septet could be due to a ^{15}NO group migrating over the six rhodium atoms seems highly improbable because the ^{13}C NMR spectrum shows the CO's to be static at room temperature.[11]

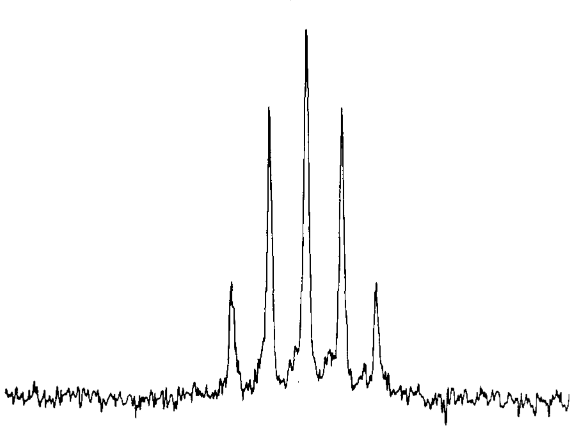

Figure 2. The ^{15}N NMR spectrum of the ^{15}N-enriched $[Rh_6N(CO)_{15}]^-$ anion.[12]

(iii) The IR spectra (of the PPN^+ salts in THF solution) show bands at 2060 (vw, sh), 2015-2010 (vs), 1895 (vw, sh), 1860 (vs), and 1830 (w) cm^{-1} for the cobalt compound, and at 2060 (vw, sh), 2025-2020 (vs), 1910 (vw, sh), 1890 (sh), 1873 (vs), and 1847 (w) cm^{-1} for the rhodium compound; these are in accord with the X-ray structure and, except for the expected shift to higher frequencies, are strictly similar to those of the $[M_6C(CO)_{15}]^{2-}$ anions, indicating an identical CO distribution.

In view of previous results[13] on the reaction of several carbonyl metalates and NOCl, the present syntheses are rather surprising (but see ref 4). The formation of interstitial nitrides could simply be explained by NO coordination followed by reduction to nitrogen by the cluster or by CO; this would be similar to the origin of the carbide atom in the high-temperature synthesis of carbido carbonyl clusters[14] and the reduction of NO_2^- to NO in the synthesis of $[Fe(CO)_3(NO)]^-$ [15] However, the synthesis of $[Rh_6N(CO)_{15}]^-$ from the reaction of $[Rh_7(CO)_{16}]^{3-}$ with CO/NO clearly requires a more complex process.

The isolation of this new class of nitrido carbonyl clusters, which are analogous to the metal interstitial nitrides, provides another example of the similarity in behavior between carbonyl clusters and metals. We also suspect that the interstitial nitrogen atom should result in increased stabilization of the cluster, as in the case of carbides, thus allowing cluster growth by thermal rearrangement.

Further work on this possibility and on the extension of the synthesis to other transition metal cluster compounds is in progress.

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(5) The crystals of the PPN^+ salt of the analogous rhodium compound are isomorphous with those of the cobalt compound, and its structure refinement is in progress.
(6) Crystal data: $C_{51}H_{30}Co_6N_2O_{15}P_2$, M 1326.4, triclinic, space group $P\bar{1}$ (No. 2), with a = 19.686 (8), b = 9.065 (5), c = 15.737 (7) Å; α = 95.69 (6), β = 69.99 (6), γ = 88.31 (6)°; D_m = 1.66 (2), D_c = 1.68 g cm^{-3}; Z = 2. Intensities were collected on an automatic diffractometer with graphite-monochromated Mo Kα radiation up to $2\sigma \leqslant 23°$. The structure was solved by conventional Patterson and Fourier methods and refined by block-matrix least squares, on the basis of 3455 independent observed reflections, to R = 0.056.
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(12) The ^{15}N NMR spectra of the Ph$_4$P$^+$ salts (^{15}N 97%) in acetone-d_6 at room temperature show resonances at −184.0 ppm ($W_{1/2} = 44$ Hz) for the cobalt compound and the central five lines of a septet at −272.6 ppm ($W_{1/2} = 1.0$ Hz) with respect to external CD$_3$^{15}NO$_2$, ^1J(Rh^{15}N) = 6.1 Hz, for the rhodium compound. Corresponding resonances are observed in the ^{14}N spectra, although the resonance of the rhodium compound shows only three poorly resolved lines of the expected septet, ^1J(Rh^{14}N) $\simeq$ 4 Hz, due to unfavorable relaxation effects.

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Chemiluminescence of Diphenoyl Peroxide. Pulsed Laser Spectrophotometric Detection of Radical Ion Intermediates on the CIEEL Path

Sir:

Our investigation of the chemiluminescence of diphenoyl peroxide (DPP) led us to postulate the chemically initiated electron-exchange luminescence (CIEEL) mechanism for that[1] and, later, for numerous other peroxides.[2] The key feature of the CIEEL mechanism is the rate-limiting single-electron transfer from the chemiluminescent activator to the peroxide to generate radical-ion intermediates from the neutral, ground-state, closed-shell reactants. These ions undergo further chemical transformations before they finally annihilate to form electronically excited states. The primary evidence for the intermediacy of the radical ions in this sequence has been the correlation of reaction kinetics with the redox properties of the reactants. We report herein the results of our pulsed laser spectrophotometric[3] study of the reaction of DPP with several electronically excited electron donors (activators). Pulse excitation enables us to identify the intermediate reaction products by their characteristic absorption spectra and also to measure the rate of the reaction. These experiments show quite clearly that radical ions are formed in the reaction of DPP with the chemiluminescence activators and that generation of caged ions precedes the formation of electronically excited products in the chemiluminescence process.

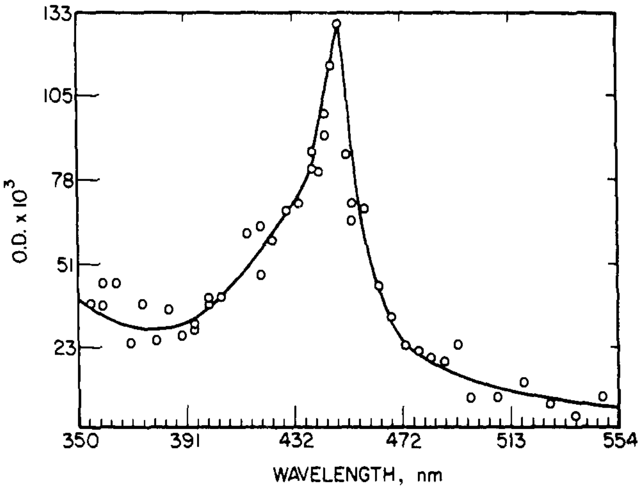

Figure 1. Absorption spectrum of pyrene radical cation recorded 200 ns after excitation. The solvent is acetonitrile, the pyrene concentration is 3.04×10^{-5} M, and the DPP concentration is 2.4×10^{-3} M.

The fluorescence of excited singlet pyrene (Py*^{1}), in acetonitrile solvent, is quenched by DPP. The yield of benzocoumarin (BC), the only volatile product of the reaction, is 60%. When Py*^{1} is generated by irradiation with the nitrogen laser, it is possible to record the absorption spectra of the transient intermediates that result from its reaction with the peroxide. The spectrum that we observed 200 ns after the excitation of the pyrene, shown in Figure 1, is identical with that which has been attributed previously to pyrene radical cation (Py$^{+}\cdot$).[4] The yield of cage escaped Py$^{+}\cdot$ can be estimated by measuring the optical density of its characteristic absorption 150 ns after the excitation when essentially all of the Py*^{1} has reacted, but well before there is any significant reaction of Py$^{+}\cdot$. The yield of cage escaped Py$^{+}\cdot$ under these conditions in acetonitrile was determined to be 5%.

We have also investigated the electron-transfer reactions of Py*^{1} with several other electron acceptors including *p*-dicyanobenzene (DCB) and phthaloyl peroxide (PP). Comparison of the yield of Py$^{+}\cdot$ from these systems with that from the Py*^{1}-DPP system is particularly revealing. Weller has shown that Py*^{1} is quenched by DCB in acetonitrile by electron transfer to generate Py$^{+}\cdot$.[5] We have determined that the yield of cage escaped Py$^{+}\cdot$ in this system is 67% of the Py*^{1} that reacts with DCB. The remaining 33% of the Py*^{1} is evidently converted into ground- or triplet-state pyrene, apparently by in cage-ion annihilation. When phthaloyl peroxide[6] reacts with Py*^{1}, we have determined that the yield of escaped Py$^{+}\cdot$ is 48%. It should be noted also, that in comparison with DPP, phthaloyl peroxide is not chemiluminescent.[7] The CIEEL mechanism provides a convincing explanation for the different behavior of phthaloyl and diphenoyl peroxides.

One-electron reduction of DPP by Py*^{1}, followed by oxygen-oxygen bond cleavage, generates diphenate radical anion. Rapid decarboxylation and ring closure of this species produces a powerful reducing agent, benzocoumarin radical anion (BC$^{-}\cdot$), presumably within the same solvent cage as Py$^{+}\cdot$. The radical-ion pair, Py$^{+}\cdot$BC$^{-}\cdot$, has several energetically possible reaction channels. Annihilation within the cage can generate singlet or triplet excited pyrene, or pyrene ground state.[8] In competition with annihilation, diffusion into bulk solution generates the low yield of escaped Py$^{+}\cdot$ that we observe. On the other hand, one-electron reduction of PP generates phthalate radical anion. The structure of this species precludes its efficient rearrangement to a powerful reducing agent. The cage annihilation reactions that consume the BC$^{-}\cdot$Py$^{+}\cdot$ pair

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