Figure 2. Plot of log k_q vs. $E^{0-0}(*D,D)$ for the energy-transfer quenching of aromatic triplets by biacetyl in benzene (A) and o-anisil in cyclohexane (B). The points represent the experimental data found in ref 23 and 16. The solid line is the best fitting curve according to eq 8 (see text).

$$\lambda = 2(\Delta G^{\ddagger}_D + \Delta G^{\ddagger}_Q) \tag{9}$$

where $\Delta G^{\ddagger}_D$ and $\Delta G^{\ddagger}_Q$ are the free activation energies of the corresponding "self-exchange" energy-transfer reactions. In the energy-transfer quenching of a homogeneous family of donors having variable excited-state energies by a single quencher, k_d, k_{-d}, k_{en}^0, λ, $E^{0-0}(*Q,Q)$, $C(*D,D)$, and $C(Q,*Q)$ are constant and eq 4 reduces to

$$\Delta G = -E^{0-0}(*D,D) + \text{constant} \tag{10}$$

Thus according to eq 8, for low $E^{0-0}(*D,D)$ values, log k_q increases linearly (slope $1/2.3RT$) as $E^{0-0}(*D,D)$ increases, while for high $E^{0-0}(*D,D)$ values log k_q reaches a plateau value equal to log k_d. Using different quenchers, the $E^{0-0}(*D,D)$ range covered by the intermediate nonlinear region becomes broader and broader as λ increases. From the best fitting procedure of eq 8 to experimental results, it is possible to obtain λ and the $E^{0-0}(*D,D)$ value which makes $\Delta G = 0$. For example, using Sandros' data for energy transfer from aromatic triplets to biacetyl ("classical" acceptor)[23] and o-anisil ("nonclassical" acceptor),[16] the best fitting procedure (Figure 2)[24] gives $\lambda = 0.3$ μm^{-1} and $\Delta G = 0$ for $E^{0-0}(*D,D)$ = 1.95 μm^{-1} in the case of biacetyl and $\lambda = 0.5$ μm^{-1} and ΔG = 0 for $E^{0-0}(*D,D)$ = 2.14 μm^{-1} for o-anisil. For biacetyl, E^{0-0} is known[23] to be 1.97 μm^{-1}, which means that in this case the C terms in eq 4 are negligible. Assuming that this is also approximately true for o-anisil, we obtain a value of ~2.14 μm^{-1} for its unknown E^{0-0} energy. The much higher λ value obtained for o-anisil is in agreement with the fact that its triplet is much more distorted than triplet biacetyl.[16]

A more detailed discussion and the application of this treatment to other "classical" and "nonclassical" energy-transfer processes[14,15,17-21] will be reported elsewhere.

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Bifunctional Activation of Carbon Dioxide. Synthesis and Structure of a Reversible CO_2 Carrier

Sir:

Unlike many other small molecules, CO_2 very rarely forms adducts with transition metals.[1,2] Formation of elusive CO_2 complexes is normally followed by ready metal-promoted elementary transformations, which include dimerization,[3] disproportionation,[3,4] and deoxygenation of CO_2.[5] So far, the presence of intact CO_2 has only been structurally verified in $(Cy_3P)_2Ni(CO_2)$ (Cy = cyclohexyl).[1]

Although it was variously suggested that metal basicity[1,2,6] is an important prerequisite to CO_2-metal adducts formation, we feel that the bifunctional nature of some metal complexes which contain transition metals in low oxidation states, along with alkali cations, could be taken into account as playing an unexpected role in CO_2 fixation. This hypothesis comes from the fact that in many simple reactions CO_2 seems to require for its activation, in addition to a basic center, the assistance of an acidic[7] partner. With this in mind, we looked for an acid-base partnership between transition and alkali ions in bimetallic complexes.

Reducing N,N'-ethylenebis(salicylideneiminato)cobalt(II), Co(salen), or a substituted Co(salen), with alkali metals (M), we generated a bifunctional complex, Co(salen)M, in which
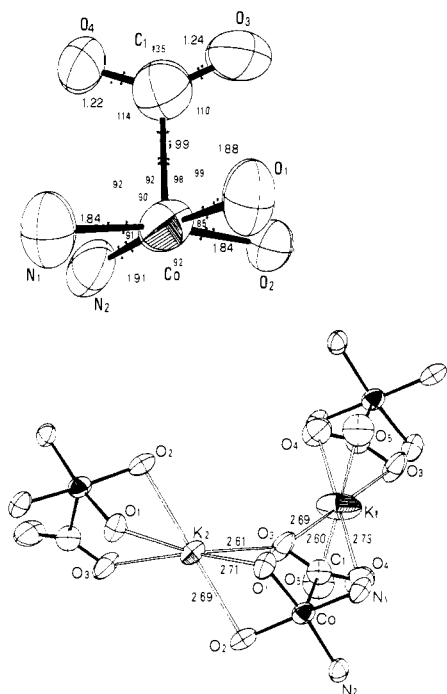
Figure 1. An ORTEP view showing the repetitive unit of the polymeric [Co(pr-salen)KCO$_2$THF]$_n$ and the coordination sphere around cobalt.[23]

both the basic cobalt(I) and the alkali cation are held close by the same ligand.[8]

Many of these complexes have been found to react with CO_2 and a few years ago we reported the isolation of a 1:1 Co-(salen)Na-CO_2 adduct.[9] The reaction between [Co(salen)M] complexes and CO_2 rarely affords suitable crystals for an X-ray analysis, whose lack, however, makes the hypothesis concerning the active sites involved in CO_2 fixation and, consequently, the bifunctional activation of CO_2, rather uncertain. We describe here the synthesis and the X-ray structure analysis of a new reversible CO_2 carrier based on the [Co(salen)M] system.

A deep green THF solution of [Co(pr-salen)K] (II) reacting with CO_2 at room temperature affords deep red crystals of [Co(pr-salen)KCO$_2$THF] (III).[10] III releases CO_2 in vacuo
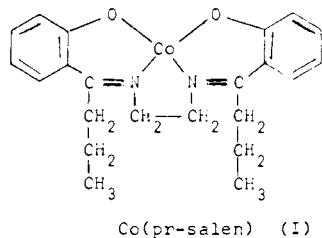
giving back the starting deep green solution. This reversibility was checked over several cycles. The crystals can be isolated working in a CO_2 atmosphere. The complex displays four sharp IR bands due to the bound CO_2 at 1650 (s), 1280 (m-s), 1215 (s), 745 (s) cm^{-1} as confirmed by isotope labeling.[11] The X-ray analysis was performed on rather poor quality crystals, since they lose CO_2 very easily. Several brown-red single crystals of III sealed in capillary glass tubes under CO_2 were mounted on a Philips PW1100 diffractometer. Crystals are monoclinic, space group $C2/c$ or Cc (the former confirmed by the struc-

tural analysis), with $a = 17.805$ (4), $b = 21.251$ (5), $c = 16.192$ (3) Å; $\beta = 112.5$ (3)° (from least-squares fitting of setting angles of 25 reflections). The density calculated for eight formula unit in the cell is $D_{calcd} = 1.325$ g cm^{-3}. Three-dimensional intensity data were collected from a crystal with dimensions 0.4 × 0.2 × 0.2 mm., employing graphite mono-chromatized Mo Kα radiation, ω-2θ scan of width 1.2°. Only 1096 independent reflections with $I \geqslant 3\sigma(I)$[12] were measured in θ range 3-25°.[13] The structure was solved by direct methods.[14] The E map computed with the 200 largest E's with signs from the set showing the highest figure of merit revealed the positions of Co and K atoms in the asymmetric unit. The structure was completed by successive Fourier syntheses and refined by full-matrix least-squares methods.[15,16] The final R[17] value was 0.085 for the observed reflections.

The structure consists of parallel chains running along the c direction. An ORTEP view[18] of the repetitive unit {[Co(pr-salen)]$_2$K$_2$THF$_2$(CO$_2$)$_2$}$_n$ forming the chains is depicted in Figure 1 and shows a selection of bond distances and angles.[19] The chains could be described as generated by the octahedra around K(1) and K(2) sharing opposite vertices through one of the CO_2 oxygen atoms. The two independent potassium ions in the asymmetric unit are at special position on the inversion center and on twofold axes, respectively. The six oxygen atoms around K(1) are provided by two CO_2 and two THF molecules, while K(2) is bound to two bidentate pr-salen units and to two oxygen atoms of two CO_2 molecules. Each CO_2 molecule shares one oxygen between two K$^+$ ions. The most important chemical features of the structure are (i) the bimetallic nature of the complex, with pr-salen acting as binucleating ligand which brings close together cobalt and potassium ions; (ii) the nearly square-pyramidal geometry around cobalt, as can be deduced from the angle values given in Figure 1 (the cobalt is displaced 0.16 Å from the best plane through O(1), O(2), N(1), and N(2) atoms; the Co-O and Co-N bond distances are in good agreement with those found for other unsubstituted Co(salen) complexes;[20] rather relevant is the Co-C(1) distance, which resembles the usual Co-C bond length found in many alkyl derivatives of Co(salen),[21,22] in which, however, cobalt attains hexacoordination); (iii) the bonding mode of the carbon dioxide (CO_2 is C bonded to cobalt and O bonded to the two different K$^+$ ions; carbon dioxide is bent, as expected from an approximate sp^2 geometry around carbon). C-O bond lengths (1.24 and 1.22 Å) must be compared with free CO_2 (1.16 Å) and with CO_2 η^2 C,O bonded in (Cy$_3$P)$_2$Ni(CO$_2$) (1.17 and 1.22 Å).[1] It must be, however, emphasized that in the nickel complex CO_2 displays a completely different anchoring mode, which results from the addition of the carbenoid metal to the activated CO bond.

This structure proves both the presence of the intact CO_2 and the "special" bonding mode of CO_2 interacting with three metal centers. This result strongly supports the hypothesis concerning the bifunctional activity of the starting Co(salen)-M-like systems; so, it is quite reasonable to suppose that CO_2 fixation by complexes like Co(salen)M involves concerted attack of the nucleophilic cobalt(I) on the electrophilic carbon of the CO_2, while the acid partner M$^+$ interacts with the basic oxygens. Another interesting aspect of this chemistry is the very easy reversible formation and cleavage of a metal-carbon σ bond.

Concluding, we feel strongly that the result described here is not only interesting in itself, but also suggests the utilization of bifunctional complexes as well as for promoting the activation of other substrates. The role of other polynucleating ligands, as well as the influence of the alkali and transition ions on the formation of CO_2 complexes, is under investigation.

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(10) A THF (100 mL) suspension of Co(pr-salen) (2.2 g, 4.95 mmol) was reacted with the stoicheiometric amount of potassium (0.2 g, 5.12 mmol). The mixture was heated at the boiling point of the THF and then was stirred vigorously for 24 h at room temperature. The deep green THF solution of [Co(pr-salen)K], upon exposure to a CO_2 atmosphere, gave on standing [Co(pr-salen)KCO$_2$THF] as deep red crystals (yield, ~75%). Calcd for [Co(pr-salen)KCO$_2$THF] ($C_{27}H_{34}N_2O_5CoK$): C, 57.44; H, 6.03; N, 4.96. Found: C, 56.48; H, 6.19; N, 4.71. The solid is stable under a CO_2 atmosphere only. It was found practically diamagnetic with a $\chi_g = 0.30 \times 10^{-6}$ cgs u at 293 K.

(11) With $^{13}CO_3{}^{2-}$ these bands are at 1610, 1250, 1192, and 732 cm^{-1}, respectively. IR data are from Nujol mulls.

(12) Standard deviations on intensity were computed as $\sigma(I) = [P + 0.25(T_p/T_B)^2(B_1 + B_2) + (0.04I)^2]^{1/2}$, where P is the total peak count in a scan of time T_p; B_1 and B_2 are the background counts each in a time T_B; I is the intensity equal to $P - 0.50(T_p/T_B)(B_1 + B_2)$.

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(15) The function minimized during least-squares refinement was $\Sigma_w(F_o - F_c)^2$, where the weighting factor w is $4F_o^2/\sigma(F_o^2)$.

(16) Owing to the large number of atoms to reflections ratio, anisotropic thermal parameters were refined only for noncarbon atoms, with the exception of the oxygen of the tetrahydrofuran group. Carbon atoms of the propylic chains of Co(pr-salen) are affected by relatively high apparent thermal motion, probably indicative of position disorder. All atoms of the tetrahydrofuran group have very high thermal parameters; this was ascribed to statistical site occupancy. Some least-squares cycles were carried out with reduced occupancy parameters. Results seem to indicate that thermal parameters assume acceptable values when the occupancy of the tetrahydrofuran group is ~50%. However, previous refinement was considered complete and adequate to reveal all structural features of chemical significance.

(17) The discrepancy index R is defined as $\Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. The scattering factors for Co, K, O, N, and C were taken from International Tables for X-ray Crystallography, Vol. III, Kynoch Press, Birmingham, 1962, p 202. To the form factors of Co a correction for anomalous dispersion ($\Delta F'$ and $\Delta F''$) was applied according to D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

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(23) O(1), O(2), N(1), and N(2) are the donor atoms of the pr-salen ligand, whose organic part has been omitted for clarity. O(3) and O(4) are the oxygens of the CO_2; O(5) belongs to a THF molecule.

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Interaction of an Aliphatic Hydrogen Atom with a Transition Metal. The First Direct Observation of a Strong C—H···Metal Interaction Derived from a Single Crystal Neutron Diffraction Study[1] of {Fe[P(OCH$_3$)$_3$]$_3$(η^3-C$_8$H$_{13}$)}$^+$[BF$_4$]$^-$

Sir:

It is generally agreed that metal-complex-induced C–H bond "activation", which is of extreme fundamental and commercial importance in homogeneously catalyzed chemical reactions,[2,3] often proceeds via a C—H···metal *intermediate* of heretofore unknown geometry.[3] Important structural questions associated with the process of C—H bond activation are (1) how much is a C—H bond stretched when the H atom interacts with a metal center, and (2) what angular deformations occur at the C atom upon formation of the C—H···M intermediate? Except for very strong B—H···Mo[4] and C—H···Mo[5,6] interactions discussed below, weak M···H interactions of ~2.6–2.9 Å derived mainly from X-ray diffraction investigations have been found in $PdI_2(PMe_2Ph)_2$,[7] $RuClH(PPh_3)_3$,[8] $Rh(SiCl_3)ClH(PPh_3)_2$,[9] [Rh(PPh$_3$)$_3$]·ClO_4·CH_2Cl_2,[10] $RuCl_2(PPh_3)_3$,[11] $Pd[PPh(t-Bu)_2]_2$,[12] and $Pt[PPh(t-Bu)_2]_2$.[12] In this regard, although numerous neutron diffraction studies of M—H and M—H—M systems have been reported,[13] *no* such studies of C—H···M systems have been reported.[31] We report the first *direct* structural observation of an unprecedentedly strong C—H···M interaction in the metal-hydrocarbon complex {Fe[P(OMe)$_3$]$_3$(η^3-C$_8$H$_{13}$)}$^+$[BF$_4$]$^-$, **1**. The neutron diffraction study of **1** was undertaken in order to precisely define the structural geometry of a possible C—H···Fe intermediate which might be a possible precursor to aliphatic C—H bond scission.
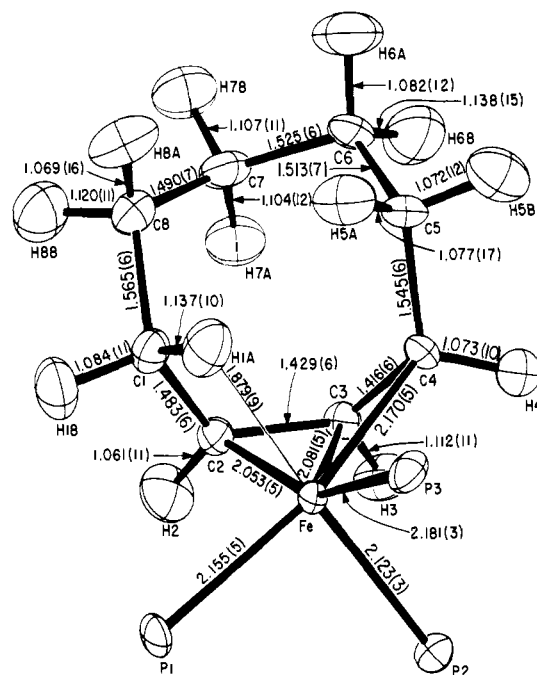
Figure 1. Atom labeling scheme for the {Fe[P(OCH$_3$)$_3$]$_3$(η^3-C$_8$H$_{13}$)}$^+$ cation (-OCH$_3$ groups omitted for clarity) showing the distorted octahedral coordination around the Fe atom with the aliphatic H atom (H(1A)) occupying a coordination site. The very strong C(1)—H(1A)···Fe interaction, in which the Fe···H(1A) distance is ~0.1 Å greater than the sum of the covalent radii, is indicated with a faint line. The thermal ellipsoids of nuclear motion for all atoms are scaled to enclose 50% probability and important internuclear distances (uncorrected for thermal motion) are given with their estimated standard deviations. The C(1)–H(1A)-Fe angle is 100.6 (6)°. The C(2)-C(1)-C(8) angle is 116.6 (4)° while the other five tetrahedral angles subtended at C(1) are in the range of 104.2–110.8°. The range of C-C-C angles for the remaining aliphatic carbon atoms is from 114.5 to 117.4°.