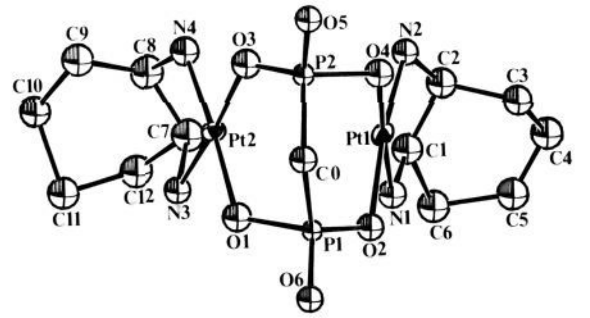

Figure 3. Structure of $[Pt_2(cis\text{-dach})_2(MDP)]$. Distances around the periphery of the Pt are as follows: Pt–N = 2.08 (3), Pt–O = 2.06 (2), O–P = 1.54 (4), Pt–C = 1.83 (2) Å. $[Pt_2(cis\text{-diaminohexane})_2(\text{methylenediphosphonate})]\cdot 9H_2O$ crystallizes in the orthorhombic space group *Iba*2, with $a = 21.67$ (1) Å, $b = 12.13$ (1) Å, $c = 23.63$ (1) Å, $V = 6209$ (6) Å^3, $Z = 8$. Automated Patterson search techniques were used to obtain the two Pt atoms, and the rest of the structure was refined to final agreement factors of $R = 3.6\%$ and $R(w) = 3.8\%$ for 1390 reflections.

rophosphate[11] complexes, and some preparative[12] and solution studies[13] of related compounds, have been published. *In this initial study, we have chosen Pt^{2+} as a useful preliminary model for Zn^{2+}*. The well-defined[14] Pt^{2+} square-planar geometry provides a valuable point of departure for evaluation of the less discriminating[14] and more elusive coordination chemistry of Zn^{2+} with phosphonate ligands. This paper describes the preparation and structure determination of three Pt^{II}(bisamine)/phosphonate complexes, $Na^+[cis\text{-}Pt(NH_3)_2(PFA)]^-$, $Na^+[Pt(dach)(PFA)]^-$, and $[Pt_2(dach)_2(MDP)]$ (dach = diaminocyclohexane).

$Na^+[cis\text{-}Pt(NH_3)_2(PFA)]^-$ was prepared by adding 20 mg of $cis\text{-}Pt^{II}(NH_3)_2Cl_2$ to a 10 mL solution of 20 mg of trisodium phosphonoformate (dark, 50 °C, 12 h), followed by concentration to about 2 mL via rotovaporation. Pale yellow plate-like crystals appeared upon slow evaporation. The structure of the $[cis\text{-}Pt(NH_3)_2(PFA)]^-$ anion is shown in Figure 1.[15] The strikingly simple structure of this compound features the expected square-planar geometry of the Pt(II) atom and the phosphoformate ligand forming a five-membered (Pt–O–C–P–O) chelate ring.

$Na^+[Pt(trans\text{-}l\text{-dach})(PFA)]^-$ is prepared by adding 20 mg of $Pt(trans\text{-}l\text{-dach})Cl_2$[16] to 10 mL of an aqueous solution containing 17.9 mg of $AgNO_3$, followed by 15.8 mg of trisodium phosphonoformate after AgCl was removed. After stirring in the dark for 12 h, the solution (pH = 5.4) was concentrated to 2 mL, and brick-like colorless crystals appeared in about 2 days. The structure of $[Pt(dach)(PFA)]^-$ is shown in Figure 2.[15] The geometry is very similar to that of the related $[cis\text{-}Pt(NH_3)_2(PFA)]^-$ complex, suggesting again a strong tendency for the five-membered (Pt–O–C–P–O) chelate ring to form.

The third complex, $[Pt_2(dach)_2(MDP)]$, was prepared under similar conditions: 27.0 mg of $Pt(cis\text{-dach})Cl_2$[16] was added to 10 mL of aqueous $AgNO_3$ (24.1 mg, dark), followed by a 5 mL solution of MDP (12.5 mg; free acid) after AgCl was removed. The pH was adjusted to 7.0 by addition of NaOH, and the mixture was stirred (30 h, room temperature, dark) and concentrated (2.5 mL). Colorless crystals formed in about 10 h upon cooling to 4 °C. The structure of the compound (Figure 3)[15] showed it to be bimetallic, in contrast to the Pt/PFA complexes. This was unanticipated: the preparative procedure described above used a 1:1 ratio of platinum/phosphonate. Each (dach)Pt fragment forms a six-membered (Pt–O–P–C–P–O) ring, and the Pt⋯Pt distance is nonbonding [3.266 (1) Å].

Our work provides direct confirmation of the proposal[6] that PFA and MDP form five- and six-membered chelate rings, respectively, with metal (II) ions, at least with Pt(II).[17] Work is currently underway on cognate phosphonate complexes of Zn^{2+}, Mn^{2+}, and Mg^{2+}. Pt^{II} (amine)$_2$(phosphonate) complexes were also selected as target molecules in recognition of a recent report that the complex $cis\text{-}[Pt(NH_3)_2(\text{cycladarine})_2Cl_2]Cl_2$ (cycladarine = carbocyclicarabinofuranosyladenine) and related compounds are active against topical herpes virus infections,[18] serving presumably as combination drugs. The possibility that appropriately designed PtL_2(phosphonate)-type complexes might prove to be active against various classes of viruses is being explored.[19]

Acknowledgment. We thank the National Institutes of Health (Grant CA-17367 to R.B.; Grants AI-21871 and AI-25697 to C.E.McK.)

Supplementary Material Available: Tables of atomic coordinates for $Na^+[cis\text{-}Pt(NH_3)_2(PFA)]^-$, $Na^+[Pt(dach)(PFA)]^-$, and $[Pt_2(dach)_2(MDP)]$ (2 pages). Ordering information is given on any current masthead page.

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Synthesis of the Transient Formyl Complex $[CH_3N(PF_2)_2]_3Co_2(CO)(CHO)^-$ and Observation of Facile Formyl Decomposition To Give the Mixed-Valence Complex $[CH_3N(PF_2)_2]_3Co_2(CO)_2^{\bullet-}$

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Metal formyl complexes continue to derive interest as plausible intermediates in the catalytic reduction of carbon monoxide to alcohols and hydrocarbons.[1] While many mononuclear formyl complexes have been prepared and isolated,[2,3] well-characterized polynuclear formyl complexes remain scarce as a result of enhanced decomposition reactivity relative to their mononuclear counterparts.

The major decomposition pathway in polynuclear formyl complexes, of which the dinuclear formyl complex $[CH_3N(P$-

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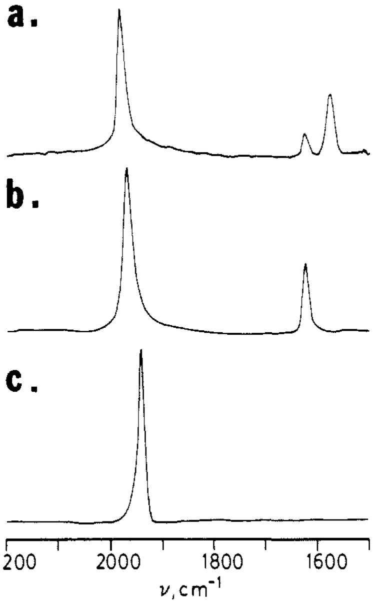
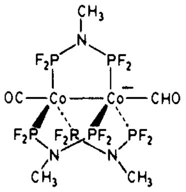


Figure 1. Infrared spectra of the carbonyl region for (a) $[CH_3N(PF_2)_2]_3Co_2(CO)(CHO)^-$ (**2**), (b) $[CH_3N(PF_2)_2]_3Co_2(CO)(CHO)^-$ (**2**) with 5 equiv of 15-crown-5, and (c) $[CH_3N(PF_2)_2]_3Co_2(CO)_2{}^{\bullet-}$ (**3**). All spectra were recorded in THF at -70 °C.

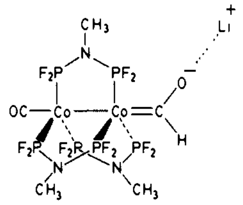
$F_2)_2]_3Co_2(CO)(CHO)^-$ (**2**) represents the simplest form, appears to involve a formyl deinsertion process[4] similar to that observed in mononuclear complexes[5,6] which may be facilitated by the presence of at least one metal–metal bond. Alternatively, evidence exists for a radical-chain decomposition pathway in certain formyl complexes,[7] but the direct observation of the pertinent paramagnetic species associated with the formyl decomposition process has not been reported until this study. Here we report our results which suggest that C–H scission of the metalloformyl bond in **2** affords the stable paramagnetic cluster $[CH_3N(PF_2)_2]_3Co_2(CO)_2{}^{\bullet-}$ (**3**).[8]

The reduction of $[CH_3N(PF_2)_2]_3Co_2(CO)_2$ (**1**)[9] with excess $LiEt_3BH$ (~2 equiv) in THF (tetrahydrofuran) at -78 °C affords an orange solution containing the cobalt formyl complex **2** in essentially quantitative yield.[10] **2** was characterized in situ by the usual spectroscopic methods. The ^1H NMR spectrum (THF-d_8) of **2** at -78 °C displayed two resonances at δ 13.2 and 2.6 in a 1:9 integral ratio for the formyl and three aminomethyl groups, respectively. When a ^{13}CO enriched sample of **1** was reduced under identical conditions and examined by ^{13}C NMR, two ^{13}C resonances in a 1:1 integral ratio were observed at δ 261 and 209.[11] The former resonance is readily assigned to the formyl moiety, while the latter resonance represents the terminal carbonyl group.[12,13] On the basis of the characteristic ^1H and ^{13}C NMR data, the product of hydride reduction is readily assigned as the anionic formyl complex **2**.

Low-temperature IR analysis (THF solvent) was next employed to further characterize **2**.[14] Figure 1a shows the IR spectrum of **2** which, interestingly enough, reveals the presence of three carbonyl stretching bands. The C–O stretching band at 1977 cm^{-1} is assigned to the lone terminal carbonyl group consistent with the ascription of **2** as an anionic complex. The remaining C–O stretches at 1622 and 1572 present in an ca. 30:70 ratio represent the solvent separated (**2a**) and ion paired formyl moiety, respectively.



2a



2b

The existence of such a contact ion pair was demonstrated by treating the reaction solution containing **2** with 5 equiv of 15-crown-5 (1,4,7,10,13-pentaoxacyclopentadecane).[15] Figure 1b shows the effect that 15-crown-5 has on disrupting the contact ion pair. The resulting two band IR spectrum reveals a growth of the 1622 cm^{-1} formyl C–O stretch, as expected, along with a slight shift of the terminal carbonyl band to 1966 cm^{-1}. The same results are also obtained when a THF solution of **1** containing 5 equiv of 15-crown-5 is treated with $LiEt_3BH$ at -78 °C. On the basis of these data we formulate the contact ion as a lithium–carbonyl oxygen bonded ion pair (**2b**). Such a contact ion pair has been observed in other anionic metal formyl and acyl complexes and is expected based on the lower formyl–carbonyl stretching frequency relative to the solvent separated ion pair.[16]

Complex **2** was observed to be stable for a period of at least 1 week when maintained at -70 °C. However, the orange color quickly changed to the characteristic green color of the radical anion **3** as the solution temperature was raised above -50 °C. This transformation was complete by -25 °C, and identity of **3** was ascertained by IR and EPR spectroscopy. Figure 1c shows a single C–O stretching band at 1940 cm^{-1} as expected for complex **3** possessing idealized D_{3h} symmetry. This ~60 cm^{-1} shift to lower frequency for the C–O stretching band of **3** relative to **1** (ν_{CO} 2007 cm^{-1}) has also been observed in the one-electron reduction of many metal clusters[17] and was readily demonstrated by reducing **1** with

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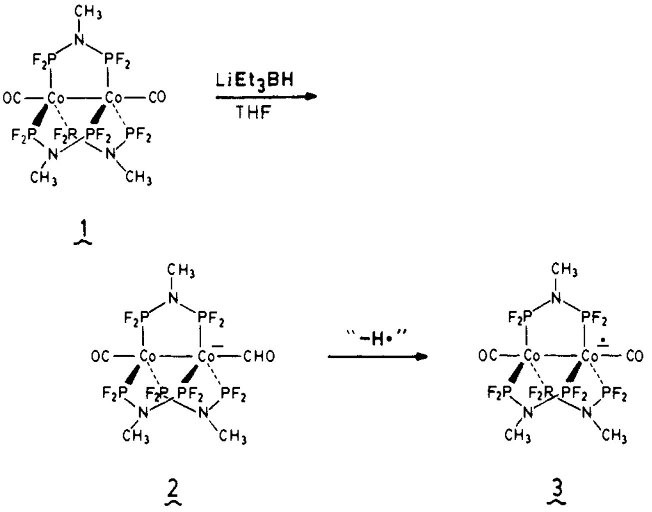
a known one-electron reducing agent. When **1** was treated with a stoichiometric amount of cobaltocene, the resulting green colored solution displayed an IR spectrum identical with that obtained from a solution containing decomposed **2**. Finally, a well-resolved EPR spectrum centered at g = 2.025 was recorded for **3** in agreement with published data.[18] The overall sequence of events is illustrated below.



The direct observation of **3** as the sole organometallic product from **2** is important as it represents the first reported paradigm of a stable paramagnetic species formed from a formyl C–H bond scission process. Moreover, **3** is of further general interest as it may be considered as a mixed-valence d^9–d^{10} complex that exhibits complete electron delocalization over both cobalt centers as required for a class III charge-transfer complex.[19] The fate of the formyl derived hydrogen atom is not known at this time, and attempts to retard the decomposition of **2** by using hydrogen atom donors such as 9,10-dihydroanthracene and tri-*n*-butyltin hydride have been unsuccessful.

We believe that the formation of the radical anion **3** (relative to other decomposition pathways) may be related to its intrinsic stability. In comparison to other known formyl complexes that decompose via a formyl C–H bond scission manifold, **3** affords the only chemically and electrochemically stable radical anion.[20] The stability of the resulting radical anion is important as it undoubtedly modulates the sequence of subsequent chemical events. Redox instability has been shown to drive the radical product of formyl decompostion in a chain propagating fashion to the corresponding metal-hydride product.[7,21] However, once formed **3** remains inert, a feature which is attributed to the redox stabilization associated with the ancillary fluorophosphine ligands.[22]

Formyl-trapping experiments and the reactions of **1** with other reducing agents, along with additional examples of cluster stabilized radical anions produced from formyl decomposition, will be reported in due course.

Acknowledgment. We thank Don Ellington for assistance with the NMR spectra and the UNT faculty research program and Robert A. Welch Foundation for financial support.

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Dioxetane Formation at a Double Bond Adjacent to Bridgehead Nitrogen: Rapid Reaction between Neostrychnine and Singlet Oxygen in a Polar Protic Medium. Evidence Against the Intermediacy of an Open Zwitterion

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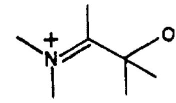
The mechanisms of reaction of $O_2(^1\Delta_g)$ with organic/biological substrates have been the subjects of considerable research effort over the last two decades.[1] Electron rich olefins, enol ethers, enamines, etc., react to give dioxetanes which can cleave to carbonyl fragments.[2-4] Much of the mechanistic discussion[5] has centered around the importance of charge-transfer interactions between the reactants and whether zwitterionic species such as **1** are intermediates on the pathway to dioxetane. Evidence for the intermediacy of open zwitterionic species has been claimed on the basis of trapping experiments in polar media where a nucleophile, most commonly, although not always, methanol as solvent, has scavenged a substrate/$O_2(^1\Delta_g)$-derived intermediate. The substrate has been either an indole[6] or an enol ether.[7] On the other hand, we have presented evidence which indicates that the reactions of such molecules with $O_2(^1\Delta_g)$ proceed via complexes which are formed rapidly and reversibly.[8] These latter species, exciplexes, must also be considered as possible precursors of both dioxetanes and the products of trapping.



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Information of pertinence to the above problem could, in principle, be available from the reactions of $O_2(^1\Delta_g)$ with relatively electron rich olefins for which formation of species of type 1 would be highly unfavorable for steric reasons; i.e., the immonium double bond would be at a bridgehead. With such considerations in mind we have examined the chemical reactivity of $O_2(^1\Delta_g)$ toward neostrychnine (**2**), a molecule in which the enamine nitrogen is indeed located at a bridgehead. This accounts for the very low pK_a of this molecule, 3.8,[9,10] and suggests that species of type **3**,

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(10) The corresponding value for strychnine (Δ^{19}-isomer of **2**) is 7.4.[9] The corresponding values for the closest available six-membered ring analogues, 1,4,5,6-tetrahydro-1,2-dimethylpyridine and 1,2-dimethylpiperidine, are 11.43 and 10.26, respectively (cf. ref 11 and references therein).

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