and characterized by ^{1}H NMR, IR, and elemental analyses.

(5) The cyclic voltammogram of a pure sample of **4a** showed a reversible wave with $E_{1/2} = +1.6$ V. This can be compared to a half-wave potential of +1.45 V for **1** (R = H). The shift to higher potential for **4a** is consistent with the strong electron-withdrawing nature of the cyano group.

(6) At present we do not have direct evidence for the elimination of a proton; however, no oxidizable form of hydrogen was observed electrochemically nor was hydrogen gas detected when the reaction was carried out in a closed system.

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Received July 9, 1979

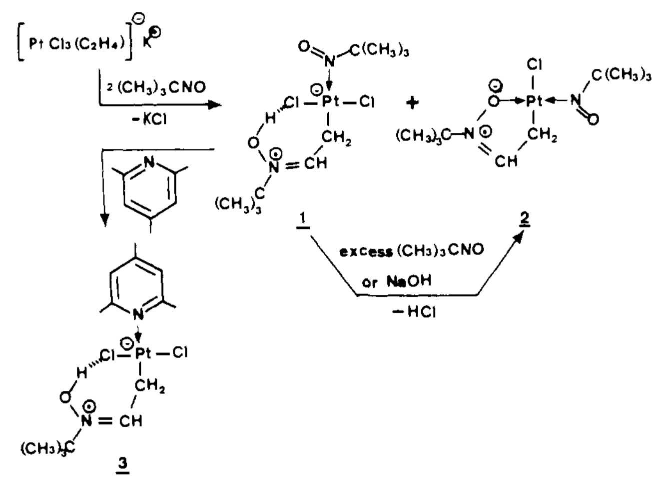
Reaction between 2-Methyl-2-nitrosopropane and Ethylene Coordinated to Platinum(II): Formation of σ-Alkyl-Nitrone Complexes

Sir:

We showed recently that 2-methyl-2-nitrosopropane (tBuNO) readily binds to platinum(II) in various complexes, through its nitrogen atom, and has a π-accepting ability intermediate between those of pyridines and ethylene.[1] Nitrosoalkanes have a nitroso group isoelectronic with dioxygen and share with it several properties as ligands of iron(II) porphyrins:[2] high affinity,[3] end-on binding[4] to the metal, and π-accepting ability.[4] Moreover an analogous similarity of bonding properties between nitroso compounds and dioxygen has been recently reported in the case of molybdenum complexes.[5] It is known that dioxygen activated by coordination to transition metals is able to react with bound olefins.[6] We now report the isolation and complete structure determination of new Pt(II) complexes resulting from the reaction between tBuNO and ethylene coordinated to Pt(II).

The reaction of Zeise's salt $[PtCl_3(C_2H_4)]K$, with 2 equiv of tBuNO in acetone at 34 °C leads to the formation of two complexes, **1** and **2**, respectively, in 90 and 10% yield according to ^{1}H NMR analysis of the solution. After a preparative reaction (500 mg of Zeise's salt, 0.32 M in acetone, 48 h), complex **1** has been found unstable in various conditions tested for its isolation (crystallization, column or thin-layer chromatography). On the contrary, complex **2**, which can be obtained from the mixture of complexes **1** and **2** in chloroform, either in 50% yield upon treatment by 2 equiv of tBuNO or in nearly quantitative yield upon treatment with aqueous NaOH, is stable and has been isolated in crystalline state (acetone-ether) as red needles, mp 187 °C. Its following characteristics—elemental analysis $C_{10}H_{21}ClN_2O_2Pt$ (C, H, Cl, N, Pt); mass spectrum M$^+$, *m/e* 432, isotopic cluster (*m/e* 431 for ^{35}Cl and ^{195}Pt); ^{1}H NMR [$CDCl_3$, $Si(CH_3)_4$, ppm] δ 1.62 and 1.70 (2 s, 2 × 9 H, $(CH_3)_3C$), 3.30 (d, $J_{H-H} = 2.7$ Hz, + dd, $J_{^{195}Pt-H} = 75$, $J_{H-H} = 2.7$ Hz, 2 H, Pt-CH_2), 6.87 (t, $J_{H-H} = 2.7$ Hz, +dt, $J_{^{195}Pt-H} = 74$, $J_{H-H} = 2.7$ Hz, 1 H, CH=); IR (KBr pellet) 1618 ($\nu_{C=N}$), 293 cm^{-1} (ν_{PtCl})[7]— are in agreement with the structure indicated in Scheme I. An X-ray crystal analysis[8] definitely establishes the structure of complex **2** (Figure 1). It displays the following salient structural features: (i) the Pt, Cl, N(11), C(3), C(4), N(5), O(6), C(7), and C(8) atoms all lie in the same plane within 0.2 Å; (ii) the Pt-C(3) [2.07 (2) Å], C(4)-N(5) [1.23 (2) Å], and N(11)-O(12) [1.22 (2) Å] bond lengths are, respectively, of the same order of magnitude as those reported for σ-alkyl-Pt(II) complexes,[9,10] for nitrones or oximes,[11] and for the complex *trans*-$[PtCl_2(tBuNO)_2]$;[1] (iii) the Pt-Cl distance [2.388 (5) Å] is also compatible with the presence of a σ-alkyl ligand trans to Cl;[9,10] (iv) the N(5)-O(6) distance [1.37 (2) Å] is larger than that found in nitrones but similar to that found in oximes.[11]

Scheme I



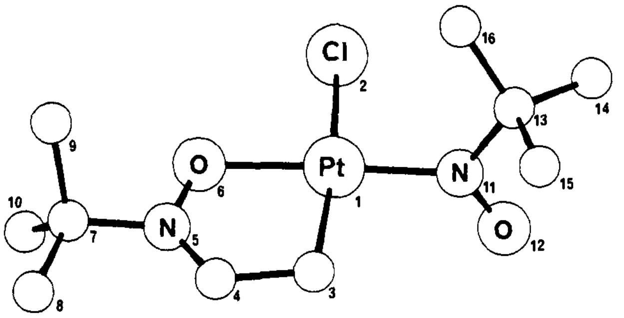


Figure 1. Molecular structure of complex **2**.[8] Typical distance not discussed in the text: Pt-N(11), 1.90 (2); Pt-O(6), 2.04 (1); C(3)-C(4), 1.50 (3) Å.

When the mixture of complexes **1** and **2**, obtained after the preparative reaction between $[PtCl_3(C_2H_4)]K$ and 2 equiv of tBuNO, is treated with 1 equiv of collidine in chloroform, a new complex, **3**, is formed and can be isolated by thin layer chromatography in 60% yield. **3** is obtained as yellow crystals (ether): mp 167 °C dec; elemental analysis $C_{14}H_{24}Cl_2N_2OPt$ (C, H, N, Cl, Pt); mass spectrum M$^+$, *m/e* 502, isotopic cluster (*m/e* 501 for ^{35}Cl and ^{195}Pt); mol wt (cryoscopy in benzene) found 532, calcd 502; ^{1}H NMR [$CDCl_3$, $Si(CH_3)_4$, ppm], collidine, 2.37 (s, 3 H, CH_3, para), 3.30 (s + d, $J_{^{195}Pt-H} = 12$ Hz, 6 H, CH_3 ortho), 6.97 (s, 2 H, H meta), σ-alkyl ligand, 1.63 (s, 9 H, $(CH_3)_3C$), 3.57 (d, $J_{H-H} = 9$ Hz, +dd, $J_{^{195}Pt-H} = 89$, $J_{H-H} = 9$ Hz, 2 H, Pt-CH_2), 7.83 (d,[12] $J_{H-H} = 9$ Hz, +dd,[12] $J_{^{196}Pt-H} = 40$, $J_{H-H} = 9$ Hz, 1 H, CH=), 8.08 (s[12] + d,[12] $J_{^{195}Pt-H} = 27$ Hz, 1 H, exchanged with D_2O, OH); IR (KBr pellet) 3450 (br, ν_{OH}), 1623 ($\nu_{C=N}$, collidine), 1595 ($\nu_{C=N}$), 318, 330, 345 cm^{-1} (ν_{Pt-Cl}); IR ($CHCl_3$ or $CHCl_3$-dioxane, 1:1) 3500 cm^{-1} (ν_{OH}, hydrogen bonded). An X-ray crystal analysis[8] establishes the structure of complex **3** (Figure 2). The main features of this structure are the following: (i) the C(3), C(4), N(5), O(6), C(7), C(10) atoms all lie in the same plane, (ii) the Pt-C(3) [2.09 (4) Å], C(4)-N(5) [1.22 (5) Å)], and N(5)-O(6) [1.44 (4) Å] bond lengths are in agreement with a σ-alkyl-nitrone moiety comparable with that found in complex **2**; (iii) the Cl(2)-O(6) distance [3.04 (3) Å] and the angle Pt-C(3)-C(4) [95° (2)], which (despite the poor precision on light atoms positions due to the presence of the platinum atom) is significantly constricted, suggest the existence of a hydrogen bond between Cl(2) and the O(6)H group. This bond could explain the peculiar 91(1)° value of the Pt-C(3)-C(4)-N(5) torsion angle. In solution the OH IR data and the observation of the ^{1}H NMR coupling constant of 27 Hz between the acidic proton of complex **3** and ^{195}Pt are also evidences for such a Pt-Cl - - H-O bond[13,14] and could

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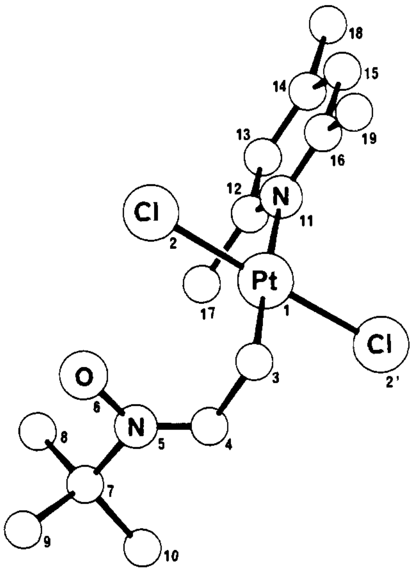

Figure 2. Molecular structure of complex **3**.[8] Typical distances not discussed in the text: C(3)-C(4), 1.53 (5); Pt-N(3), 2.15 (3) Å. Angles: C(3)-C(4)-N(5), 120 (3); C(4)-N(5)-O(6), 126 (3); N(5)-O(6)-Cl(2), 98 (3)°.

indicate the existence of a priviledged conformation of complex **3** similar to that observed in the crystalline state (Scheme I).

The ^{1}H NMR spectrum of complex **1** [$CDCl_3$, $Si(CH_3)_4$ ppm]—δ 1.63 and 1.72 (2 s, 2 × 9 H, $(CH_3)_3C$), 3.50 (d $J_{H\text{-}H}{}^9$ = Hz, +dd, $J_{^{195}Pt\text{-}H} = 84$, $J_{H\text{-}H} = 9$ Hz, 2 H, Pt-CH_2), 7.77 (d,[12] $J_{H\text{-}H} = 9$ Hz, +dd,[12] $J_{^{195}Pt\text{-}H} = 33$, $J_{H\text{-}H} = 9$ Hz, 1 H, CH═), 8.15 (s[12] + d,[12] $J_{^{195}Pt\text{-}H} = 25$ Hz, 1 H, exchanged with D_2O, OH)—is very similar to that of complex **3,** the signals of the collidine ligand being replaced by those of coordinated tBuNO (1.72, s, 9 H). Therefore complex **1** is very probably transformed into complex **3** upon ligand exchange between the coordinated tBuNO and the collidine added to the mixture of complexes **1** and **2** (vide supra) (Scheme I). The unstability of complex **1** compared with complex **3** should derive from the larger trans labilizing ability of the tBuNO ligands compared to collidine,[1] therefore favoring its cis position relative to a strongly labilizing alkyl ligand. The isomerization of complex **1** in the presence of excess tBuNO, leading to the corresponding *cis*-dichloro complex, should increase the lability of the chloride ligands and favor HCl elimination and the formation of complex **2.**

The formation of complexes **1** and **2** is the first example of a reaction between a nitrosoalkane and ethylene coordinated to a transition metal. The reactions of nitrosoalkanes and -arenes with olefins are not yet fully understood.[15] Since a simple addition of free tBuNO to coordinated ethylene is unlikely, because nitrosoalkanes are not known to exhibit a nucleophilic reactivity,[16] the reported reaction could occur between ethylene and tBuNO both activated by platinum. The mechanism and possible developments of this reaction, which leads to a double functionalization of ethylene, are under study.

Acknowledgments. M.D. thanks the Delegation Generale a la Recherche Scientifique et Technique for a fellowship. The chemical work has been supported by the Centre National de la Recherche Scientifique, ATP Grant No. 2647. We thank Dr. C. Pascard for X-ray diffractometer facilities and Engelhard Industries (France) for a loan of platinum salt.

Supplementary Material Available: Atomic fractional coordinates and thermal parameters (Table 1), anisotropic thermal parameters of heavy atoms (Table 2), and interatomic distances and angles of complexes **2** and **3** (3 pages). Ordering information is given on any current masthead page.

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Received July 2, 1979

Dioxygen Ligand Transfer. Synthesis and Rearrangement of a Heterobimetallic Dioxygen Adduct

Sir:

Considerable research has recently been devoted to dioxygen complexes of transition metals and in particular to the equilibrium involving the absorption-desorption of molecular oxygen.[1-5] Very little has been done, however, on the process of transferring the dioxygen ligand to a third entity. We now report a case in which the transfer of molecular oxygen from one metal (Co) to another (Mo) can be followed.

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