products were isolated in a liquid nitrogen cooled trap. Analysis by GC-MS revealed only two major components, methoxysilane **4** and **1** in a 1:12.5 ratio. Both components had identical retention times and mass spectra with those of authentic samples. Silatoluene (**2**) was stable to UV irradiation in the argon matrix. Warming the matrix produced a polymer which we did not characterize.

Acknowledgment. A grant from the Dow-Corning Corporation provided partial support of this work at Iowa State University. Grant CH9-00964 from the National Science Foundation supported the work at UCLA.

References and Notes

(1) Portions of this work have been presented at the A. C. Cope Award Symposium, 176th National Meeting of the American Chemical Society, Miami, Fla., Sept 1978 (O. L. Chapman), and in a plenary lecture at the 5th International Symposium on Organo-Silicon Chemistry, Karlsruhe, West Germany, Aug 1978 (T. J. Barton).

(2) Barton, T. J.; Burns, G. T. *J. Am. Chem. Soc.* **1978**, *100*, 5246.

(3) Block, E.; Revelle, L. K. *J. Am. Chem. Soc.* **1978**, *100*, 1630–1632.

(4) Dewar, M. J. S.; Lo, D. H.; Ramsden, C. A. *J. Am. Chem. Soc.* **1975**, *97*, 1311–1318.

(5) Spectral data: NMR (CCl_4) δ 0.12 (s, 3 H, SiMe), 0.57 (s, 3 H, SiMe), 0.80 (d, J_{de} = 6 Hz, collapses to s with $h\nu$ at δ 6.04, 1 H_d), 3.66 (overlapped d of d of d of d, 1 H_a, $J_{ab} \sim J_{ab'} = 7$, $J_{ac} \sim J_{ac'} = 2$ Hz, collapses to broad s with $h\nu$ at δ 7), 6.04 (d of d, $J_{ef} = 10$, $J_{de} = 6$ Hz, collapses to d with $h\nu$ at δ 0.8, 1 H_e), 7.09 and 6.93 (each d of d, $J_{bc} \sim J_{b'c'} = 12$ Hz, each collapses to a d with $h\nu$ at δ 3.66, 1 H_b and 1 $H_{b'}$), 6.60 (d of d, $J_{gi} = 6$, $J_{fg} = 14$ Hz, 1 H_g), 5.52–5.93 (partially resolved m, 4 H, H_c, $H_{c'}$, H_i, H_f); mass calcd for $C_{12}H_{16}Si_2$ 216.07906, measured *m/e* 216.07909, base peak *m/e* 108.

(6) Professor H. Bock has now obtained the photoelectron spectrum of **2** in the gas phase (private communication).

(7) The UV bands observed for **2** under conditions for maximum resolution are at 3228, 3225, 3221.5, 3218, 3214, 3210, 3185, 3181.5, 3178, 3163, 3160, 3156.5, 3153.5, 3149.5, 3139, 3135, 3132, 3129, 3124.5, 3120, 3115.5, 3095.5, 3093, 3090, 3086.5, 3078.5, 3075, 3071.5, 3069, 3065.5, 3062.5, 3060, 3054, 3050.5, 3046.5, 3042, 3039, 3012, 2998, 2973, and 2935 Å. Figure 2 shows the UV spectrum under lower resolution conditions to save space.

(8) Schlegel, H. B.; Coleman, B.; Jones, J., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 6499–6501.

(9) Spectral data: NMR (CCl_4) δ 0.17 (s, 3 H, SiMe), 1.56 (m, 2 H, $SiCH_2C{=}$), 3.37 (s, 3 H, OMe), 5.95 (m, 3 H, vinyl), 6.95 (m, 1 H, vinyl); mass calcd for $C_7H_{12}SiO$ 140.0658, measured *m/e* 140.0652.

(10) Comparison of the relative intensities of the *m/e* 141 and 126 (loss of methyl) ions shows 93% deuterium incorporation; calcd for $C_7H_{11}DSiO$ 141.07202, measured *m/e* 141.07203.

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Conversion of the Cyanocyclohexadienyl Ligand in the Cation $[(\eta^5\text{-RC}_6\text{H}_5\text{CN})\text{Mo}(\mu\text{-SMe})_4\text{Mo}(\eta^6\text{-RC}_6\text{H}_5)]^+$ (R = H or Me) into a π-Cyanoarene Ligand. Electrochemical Evidence for a Two-Electron Oxidation–Proton Elimination Mechanism

Sir:

The addition of a nucleophile to a π-complexed arene ligand to give a cyclohexadienyl transition metal complex is a well-established reaction.[1] Further reaction with a strong oxidizing agent in the case of cyclohexadienyl complexes derived from a carbon nucleophile has proved useful for the synthesis of free, substituted arenes.[2] The latter reaction suggested to us that complexes containing a substituted π-arene ligand might also be synthesized by the oxidation of a cyclohexadienyl complex under controlled conditions. Such a reaction would be useful for the synthesis of substituted π-arene complexes not obtainable by conventional methods and might also lead to the establishment of a general mechanism for the direct nuclear substitution of arenes catalyzed by transition metal complexes. We report here the novel conversion of a cyanocyclohexadienyl ligand in the cation $[(\eta^5\text{-RC}_6\text{H}_5\text{CN})\text{Mo}(\mu\text{-SMe})_4\text{Mo}(\eta^6\text{-RC}_6\text{H}_5)]^+$ (R = H or Me) into a π-cyanoarene ligand along with electrochemical evidence for a two-electron oxidation–proton elimination mechanism.

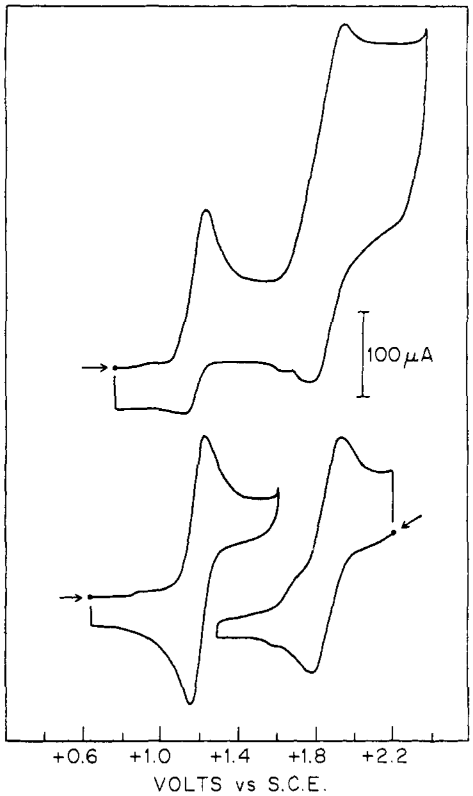

Figure 1. Cyclic voltammogram for the oxidation of $[(\eta^5\text{-C}_6\text{H}_6\text{CN})\text{Mo}(\mu\text{-SMe})_4\text{Mo}(\eta^6\text{-C}_6\text{H}_6)]^+$ in 0.1 M $(Et_4N)PF_6$-propylene carbonate at Pt vs. SCE (25 °C). The scan rate is 200 mV/s.

The previously reported cation $[(\eta^6\text{-RC}_6\text{H}_5)\text{Mo}(\mu\text{-SMe})_4\text{Mo}(\eta^6\text{-RC}_6\text{H}_5)]^{2+}$ (R = H or Me) (**1**)[3] adds 1 equiv of the sodium salts of the nucleophiles $^-$CN and $^-$OMe in acetonitrile solution affording a stable cation of the type $[(\eta^5\text{-RC}_6\text{H}_5\text{Nu})\text{Mo}(\mu\text{-SMe})_4\text{Mo}(\eta^6\text{-RC}_6\text{H}_5)]^+$ (**2**) in essentially quantitative yield.[4]

The cyclic voltammogram of **2** (R = H; Nu = CN) at a platinum electrode in propylene carbonate with $(Et_4N)PF_6$ as supporting electrolyte is shown in Figure 1. A partial scan (lower curve) shows a reversible oxidation wave with $E_{1/2}$ = +1.17 V vs. SCE. Coulometry showed that this wave is associated with a one-electron transfer. Exhaustive electrolysis of the cyanide adduct at a controlled potential of +1.3 V in propylene carbonate gave a dark red solution which on standing for several hours at 25 °C reverted back to the original orange color. A cyclic voltammetry investigation on the solution immediately after exhaustive electrolysis indicated that the oxidation product $[(\eta^5\text{-RC}_6\text{H}_5\text{CN})\text{Mo}(\mu\text{-SMe})_4\text{Mo}(\eta^6\text{-RC}_6\text{H}_5)]^{2+}$ (**3**) has a half-life of at least 1 h at 25 °C. Workup of the solution after the red color had disappeared afforded **1** in high yield along with ~0.5 equiv of HCN which was distilled from the solvent on a high vacuum line and identified by its mass spectrum. The above observations are consistent with a mechanism in which a cyano radical is slowly eliminated from **3** giving **1**. Hydrogen abstraction from the solvent by the reactive cyano radical would then account for the HCN formed. IR studies showed that small quantities of solid cyano compounds are also formed in the reaction; however, these products have not yet been identified. A second one-electron

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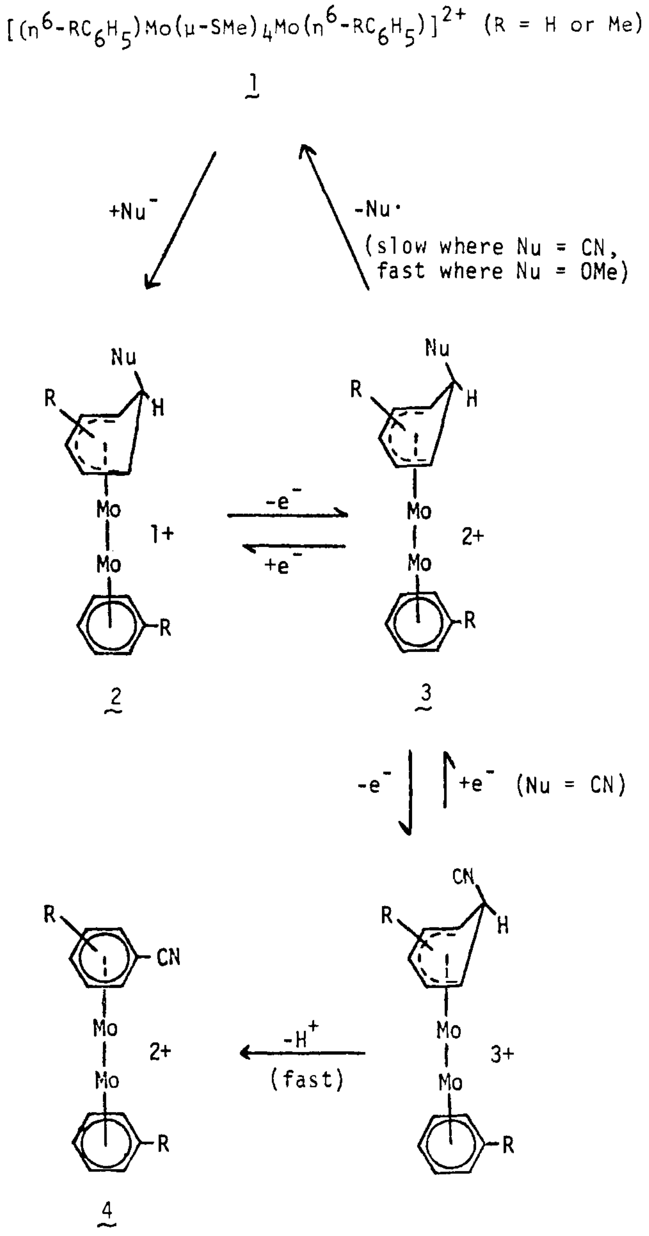
Scheme I



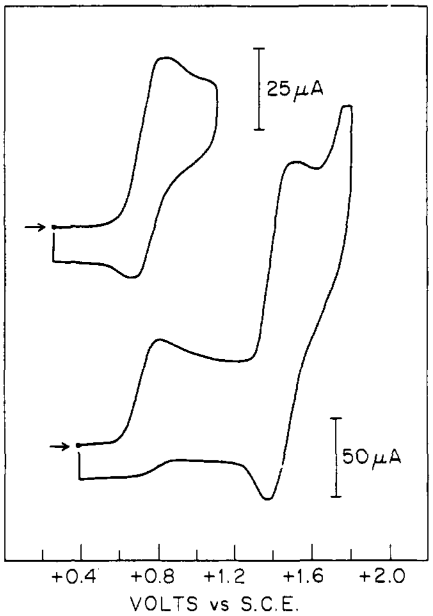


Figure 2. Cyclic voltammogram for the oxidation of $[(\eta^5\text{-}MeC_6H_5OMe)Mo(\mu\text{-}SMe)_4Mo(\eta^6\text{-}MeC_6H_5)]^+$ in 0.1 M $(Et_4N)PF_6$-propylene carbonate at Pt vs. SCE (−25 °C). The scan rate is 200 mV/s.

oxidation wave with partial reversibility is observed (Figure 1) with $E_{1/2} = +1.9$ V vs. SCE. When the scan is initially run cathodically starting at +2.2 V and reversed near +1.3 V, a new wave is observed as a shoulder on the +1.9-V wave with $E_{1/2} \simeq +1.6$ V. Exhaustive electrolysis at a controlled potential of +2.2 V in propylene carbonate showed that the new wave is due to the π-cyanobenzene complex $[(\eta^6\text{-}C_6H_5CN)Mo(\mu\text{-}SMe)_4Mo(\eta^6\text{-}C_6H_6)]^{2+}$ (**4a**) which is obtained in ~90% yield on workup of the solution.[5] Similar results were observed for the cyano derivative **2** where R = Me. The reaction appears to involve the fairly rapid elimination of a proton from the cyanocyclohexadienyl ligand in the cation $[(\eta^5\text{-}RC_6H_5CN)Mo(\mu\text{-}SMe)_4Mo(\eta^6\text{-}RC_6H_5)]^{3+}$ yielding the π-cyanoarene complex directly.[6] The proposed overall mechanism is shown in Scheme I.

Solution ^1H NMR studies on the cation $[(\eta^6\text{-}MeC_6H_4CN)Mo(\mu\text{-}SMe)_4Mo(\eta^6\text{-}MeC_6H_5)]^{2+}$ (**4b**) indicate the presence of two isomers of the η^6-MeC_6H_4CN ligand in the ratio of ~3:1. The products of the decomposition of **4b** with Na/Hg in acetonitrile-d_3 have been studied after distillation of the resultant solution into an NMR tube. The ^1H NMR spectrum showed the presence of toluene along with a smaller quantity of p-MeC_6H_4CN. No other compounds were observed. Unfortunately, the free cyanotoluene compounds are decomposed under the reaction conditions employed for their generation so that we are presently unable to determine the complete isomer distribution in **4b**.

In an attempt to extend the arene substitution reactions observed for cyanide ion to other types of nucleophiles, we have investigated the electrochemistry of the methoxy derivative of **2** (R = Me). A cyclic voltammetric study in propylene carbonate at 25 °C showed an oxidation wave of low reversibility with $E_{1/2} \simeq +0.8$ V vs. SCE. The reversibility is somewhat improved at −25 °C (Figure 2). Coulometry showed that the first oxidation wave is due to a one-electron transfer. A second oxidation wave is observed (Figure 2) with $E_{1/2} = +1.45$ V which is very close to the half-wave potential for the unsubstituted π-toluene cation (**1**). Exhaustive electrolysis at a controlled potential of +1.8 V in propylene carbonate at 25 °C gave **1** in high yield. No substitution products were obtained. These observations are consistent with a mechanism in which elimination of the methoxy group as a radical species occurs so rapidly that a two-electron oxidation intermediate cannot form (Scheme I).

The above results demonstrate that, through the appropriate choice of nucleophile and oxidation conditions, it is possible to substitute directly a π-arene ligand resulting in a stable arene-metal complex. The two-electron oxidation-proton elimination mechanism described here may also serve as a model for the reaction steps which preceed elimination of the substituted arene ligand in well-known reactions involving the oxidation of cyclohexadienyl complexes of Cr, Mn, and Fe.[2] We are presently extending our investigations to a variety of nucleophiles to determine what factors govern the stability of the cyclohexadienyl intermediates required for the formation of substituted π-arene complexes.

References and Notes

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(3) W. E. Silverthorn, C. Couldwell, and K. Prout. *J. Chem. Soc., Chem. Commun.*, 1009 (1978).

(4) All of the stable cations reported here have been isolated as their PF_6^- salts

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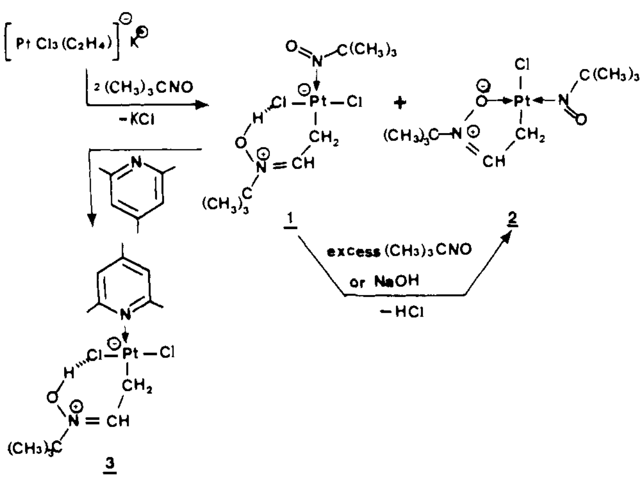
Reaction between 2-Methyl-2-nitrosopropane and Ethylene Coordinated to Platinum(II): Formation of σ-Alkyl-Nitrone Complexes

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



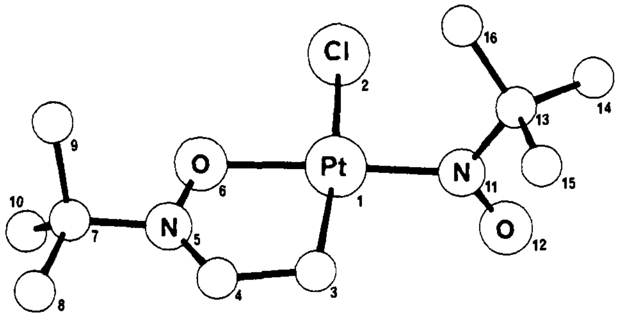


Figure 1. Molecular structure of complex **2**.[8] Typical distance not discussed in the text: Pt-N(11), 1.90 (2); Pt-O(6), 2.04 (1); C(3)-C(4), 1.50 (3) Å.

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