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Nitrosyl, Nitro, and Nitrato Complexes of Palladium(IV). The First Structurally Characterized Mononuclear Nitrosyl Complex of Palladium

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Summary: A series of $Pd^{IV}-(NO_x)$ *complexes* ($x = 1$, *nitrosyl;* $x = 2$, *nitro;* $x = 3$, *nitrate) has been synthesized. The nitrosyl derivative* $[\overline{\mathit{Pd}(CH_2CMe_2\text{-}o\text{-}C}_6H_4)(\kappa^3\text{-}Tp)(NO)]$ *is the first palladium mononuclear derivative to be structurally characterized by X-ray diffraction methods.*

The study of the interaction of nitric oxide with transition metals is one of the most important aspects of the chemistry of NO.[1] Interest in M−NO systems stems from the importance of NO in biochemical processes[2] and from the expectation that knowledge of the interaction of nitric oxide with metal surfaces, and with metal cations inside zeolite cages and related materials, may allow the design of effective catalysts for the reduction of the atmospheric pollution caused by nitric oxides.[3] Recently, the first nitrosyl complexes of group 5 elements have been structurally characterized.[4,5] They add to the wealth of information that exists on M−NO compounds of group 6−9 elements,[1] leaving those of group 10 as a comparatively poorly developed family of metal nitrosyls. Some Ni and Pt nitrosyls have been characterized by X-ray methods.[6] However, to our knowledge only the structures of a few inorganic polynuclear nitrosyl complexes have been authenticated by X-ray studies.[7] We now report the synthesis and reactivity of the new palladium nitrosyls $[\overline{\text{Pd}(CH_2CMe_2\text{-}o\text{-}C}_6H_4)(\kappa^3\text{-}Tp')(NO)]$ (Tp′ = hydrotris(pyrazolyl)borate ligand; Tp′ = Tp (**2a**), $TpMe_2$ (**2b**)) along with a single-crystal X-ray investigation of compound **2a**, which reveals it contains a strongly bent nitrosyl ligand. Related nitrate and nitro compounds **3**−**5** are also reported.

Similarly to related palladacycles,[8] the anionic derivatives $[(K)[\overline{\text{Pd}(CH_2CMe_2\text{-}o\text{-}C}_6H_4)(\kappa^2\text{-}Tp')]]$ (Tp′ = Tp (**1a**), $TpMe_2$ (**1b**)) are excellent precursors for the synthesis of Pd^{IV}−alkyl (or aryl) compounds.[9] In the present work, treatment of **1a** or **1b** (prepared in situ from the cyclooctadiene complex $[\overline{\text{Pd}(CH_2CMe_2\text{-}o\text{-}C}_6H_4)(cod)]$[10] and KTp′) with 1 equiv of Diazald (*N*-methyl-*N*-nitroso-*p*-toluensulfonamide) produces orange-red mixtures from which the new Pd−NO complexes **2a** and **2b** can be isolated after appropriate workup (Scheme 1).[11]

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[11] A 1.73 g amount of $[\overline{\text{Pd}(CH_2CMe_2\text{-}o\text{-}C}_6H_4)(cod)]$ (5 mmol) and 1.26 g of KTp (5 mmol) are dissolved in 120 mL of CH_2Cl_2, and the mixture is stirred at room temperature for 1 h. The solution is then cooled to −80 °C, and a solution of 1.07 g of Diazald (5 mmol) in CH_2Cl_2 is added dropwise. The cooling bath is removed and the reaction mixture stirred at room temperature for 3 h. The solvent is removed under reduced pressure, leaving an orange-red residue that is extracted with Et_2O, affording an orange solution. The solvent is removed again under vacuum. Complex **2a** can be purified by column chromatography, under an inert atmosphere, using a mixture of Et_2O and hexane (15:85) as the mobile phase, and it is isolated as a yellow solid. Yield: 65%. Anal. Calcd for $C_{19}H_{22}BN_7OPd$: C, 47.38; H, 4.60; N, 20.36. Found: C, 47.72; H, 4.71; N, 20.27. IR (Nujol mull): $\nu(BH)$ 2480 cm^{-1}, $\nu(N{=}O)$ 1650 cm^{-1}. Complex **2b** was similarly prepared and crystallized from acetonitrile in 60% yield. Anal. Calcd for $C_{25}H_{34}BN_7OPd$: C, 53.07; H, 6.06; N, 17.33. Found: C, 52.44; H, 6.05; N, 17.28. IR (Nujol mull): $\nu(B{-}H)$ 2520 cm^{-1}, $\nu(N{=}O)$ 1660 cm^{-1}.

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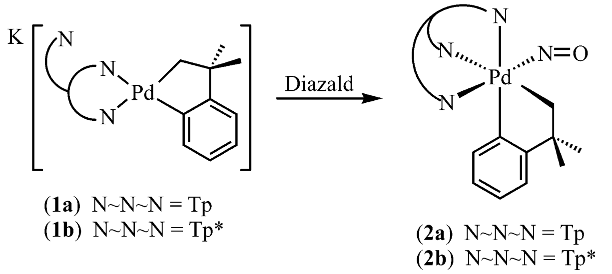
Scheme 1



(**1a**) N~N~N = Tp
(**1b**) N~N~N = Tp*

(**2a**) N~N~N = Tp
(**2b**) N~N~N = Tp*

The Tp species **2a** may also be obtained by the reaction of **1a** with [NO][BF_4], but this procedure has poor reproducibility. The two nitrosyls are yellow to red crystalline solids, soluble in common organic solvents. They exhibit moderate thermal stability and in the solid state resist the action of air for a short period of time. Details of their synthesis and properties can be found in the Supporting Information. Spectroscopic data are consistent with the structure of compounds **2** represented in Scheme 1. Tridentate coordination of the Tp′ ligand is inferred from the application of both the infrared[12] and the $\delta(^{11}B\{^1H\})$ NMR[13] criteria. The asymmetry of the metal center causes the appearance of three sets of resonances for the inequivalent pyrazolyl rings, and it is also responsible for the diasterotopic nature of the CH_2 (and CMe_2) protons of the palladacyclic unit (for instance, doublets at δ 4.00 and 4.55 ppm, $^2J_{HH} = 8$ Hz, are found for the CH_2 protons of **2a**, and singlets at 1.01 and 1.36 ppm for the Me groups). In the IR spectrum a strong absorption centered at 1650 cm^{-1} (**2a**) or 1660 cm^{-1} (**2b**) reveals the presence of a coordinated molecule of nitric oxide.

Following the Enemark−Feltham notation for the description of the MNO geometry,[14] complexes **2** can be described as $\{Pd(NO)\}^8$ systems, and therefore a bent geometry may be anticipated for their Pd−NO moiety. The above ν(NO) values, albeit not unequivocal (ν(NO) for **2** is in the range of overlap of linear (ca. 1900−1600 cm^{-1}) and bent (ca. 1750−1600 cm^{-1}) MNO groups[1]), are consistent with this proposal. The oxidation-state formalism also appears useful for these Pd nitrosyls; therefore, complexes **2** can be formulated as Pd(IV) species with a bent NO group (formally NO^-). Structural confirmation has been achieved by an X-ray study of the Tp derivative **2a**.

Figure 1 shows the solid-state molecular structure of this complex.[15] As advanced, the geometry of the metal center is essentially octahedral, with tridentate facial coordination of the Tp ligand. The two Pd−C bonds have similar lengths, although Pd1−C6 (2.016(5) Å) is somewhat shorter than Pd1−C1 (2.063(5) Å), as a consequence of the different hybridization of the two carbon atoms. The nitrosyl ligands is bonded through the N atom. It has a Pd−NO distance of 2.016(5) Å, and it is distinctively bent, with a Pd−N−O angle of 118.3(5)°. The N1−O1 distance of 1.151(7) Å is comparable to corresponding distances in other angular nitrosyls.[1,16]

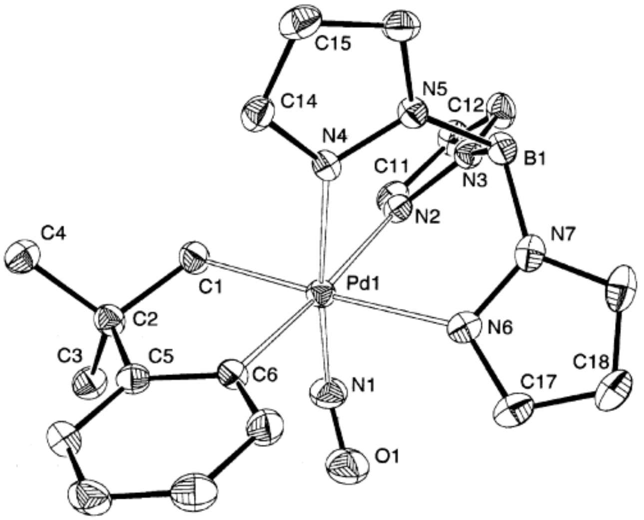


Figure 1. ORTEP diagram of complex **2a**. Selected bond distances and angles: N1−O1 = 1.151(7) Å, Pd1−N1 = 2.016(5) Å, Pd1−N2 = 2.173(4) Å, Pd1−N4 = 2.191(4) Å, Pd1−N6 = 2.191(5) Å, Pd1−C1 = 2.063(5) Å, Pd1−C6 = 2.016(5) Å; Pd1−N1−O1 = 118.3(5)°, N1−Pd1−N4 = 172.8(2)°, C1−Pd1−C6 = 81.3(2)°.

The structure of the palladium nitrosyls has also been investigated using density functional theory (B3LYP/LANL2DZ*), employing $Pd(CH_3)_2(\kappa^3\text{-}Tp')(NO)$ as model complexes (Tp′ = Tp, $TpMe_2$). The calculated structures (see the Supporting Information) reproduce accurately the experimental data obtained for **2a**. For instance, the computed Pd−NO distance (2.010 Å) and Pd−N−O angle (118°) for the Tp model compound compare well with the experimental values found for **2a** (see Figure 1).

A number of transition-metal nitrosyl complexes react with dioxygen to yield nitro or nitrate compounds.[1,17] The Pd nitrosyl **2b**, which contains the bulky $TpMe_2$ ligand, undergoes a very complex reaction with O_2 that gives an intractable mixture of products. Differently, the reaction of **2a** with dioxygen allows isolation (ca. 50% yield) of the Pd^{IV}−nitrate **3a** (Scheme 2).[18] Mechanistic studies on this transformation are hampered by its complexity, as other as yet unidentified products are generated as well. Compound **3a** behaves as a nonelectrolyte, with good solubility properties in aromatic hydrocarbons, diethyl ether, THF, and CH_2Cl_2. IR bands at 1500, 1275, and 985 cm^{-1}, attributable to NO_3 vibrational modes,[19] confirm the presence of a coordinated NO_3^- group. Additionally, treatment of a toluene

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[12] Akita, M.; Ohta, K.; Takahashi, Y.; Hikichi, S.; Moro-oka, Y. *Organometallics* **1997**, *16*, 4121.

[13] Northcutt, T. O.; Lacchicotte, R. J.; Jones, W. D. *Organometallics* **1998**, *17*, 5148.

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[15] Crystal data for **2a** at 293 K: $C_{19}H_{22}BN_7OPd$, fw 481.65, monoclinic, space group $P2_1/n$, $a = 8.114(3)$ Å, $b = 17.515(5)$ Å, $c = 14.816(5)$ Å, $\alpha = 90°$, $\beta = 104.02(5)°$, $\gamma = 90°$, $V = 2042.9(12)$ Å, $Z = 4$. The final R factor was 0.0497 for 3855 independent reflections with $I > 2\sigma(I)$ (wR2 = 0.1410). GOF = 1.066.

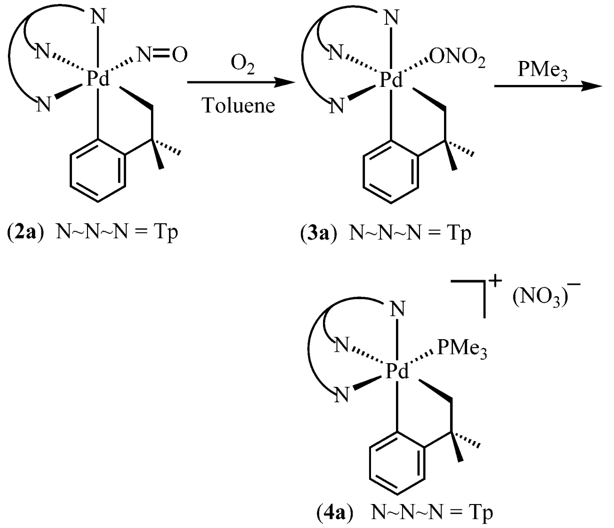
[16] Cambridge Structural Database System, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, U.K.

[17] Ford, P. C.; Lorkovic, I. M. *Chem. Rev.* **2002**, *102*, 993.

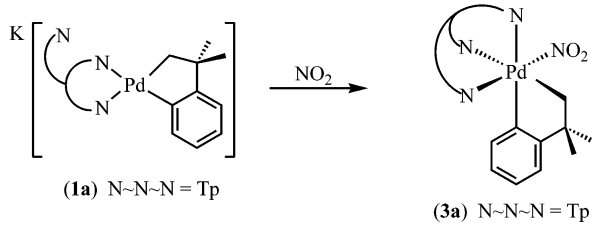
[18] Oxygen is bubbled through a solution of 482 mg of **2a** (1 mmol) in 50 mL of toluene. After 10 min the solution is taken to dryness and the solid residue extracted with 50 mL of Et_2O. Complex **3a** is obtained as yellow-orange crystals by adding hexane to a concentrated Et_2O solution and cooling at −30 °C. Yield: 50%. Anal. Calcd for $C_{19}H_{22}BN_7O_3Pd$: C, 44.43; H, 4.32; N, 19.09. Found: C, 44.63; H, 4.29; N, 19.23. IR (Nujol mull): ν(BH) 2515 and 2490 cm^{-1}, $\nu(NO_3)$ 1500, 1275, and 985 cm^{-1}.

[19] Nakamoto. K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed.; Wiley: New York, 1997.

Scheme 2



Scheme 3



solution of **3a** with 1 equiv of PMe_3 causes immediate precipitation of the cationic Pd(IV) complex **4a**, which possesses a coordinated molecule of PMe_3 in place of the nitrate. The noncoordinated NO_3^- group of **4a** gives rise to an intense absorption band at 1375 cm^{-1}, assignable to $\nu_{as}(NO_3)$.[20]

The reaction of **2a** with O_2 to give **3a** provides no evidence for the formation of a nitro compound intermediate. Nevertheless, we have succeeded in preparing such a derivative, **5a**, by means of the alternative synthetic procedure summarized in Scheme 3: namely, by NO_2 oxidation of the Pd(II) species **1a**.[21] The NMR parameters of **5a** show the expected similarity with those of **3a** (for instance, the $Pd-CH_2$ carbon of the metallacyclic linkage resonates at δ 74.9 and 75.4 ppm for **3a** and **5a**, respectively). Furthermore, observation of two IR bands at 1445 and 1325 cm^{-1} due to $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$, respectively, suggests the presence of the N-bound (i.e. nitro) NO_2^- ligand.[20] Failure to convert **5a** into **3a** in the presence of O_2 demonstrates that the former is not an intermediate in the conversion of nitrosyl **2a** into nitrate **3a** represented in Scheme 2.

In summary, we have prepared the first $\{Pd(NO)\}^8$ compounds and succeeded in characterizing for the first time by X-ray crystallography a nitrosyl complex of palladium, namely $[Pd(CH_2CMe_2\text{-}o\text{-}C_6H_4)(\kappa^3\text{-}Tp)(NO)]$ (**2a**). Its oxidation with dioxygen yields the $Pd^{IV}-$nitrate **3a** in a complex reaction that does not proceed through the related $Pd^{IV}-NO_2$ derivative **5a**. The latter compound has actually been prepared by a redox process involving NO_2 and the Pd(II) compound **1a**.

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Supporting Information Available: Text giving experimental procedures and characterization data for all new complexes and tables giving computational data and X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley: New York, 1999.

(21) A 346 mg portion of $[Pd(CH_2CMe_2\text{-}o\text{-}C_6H_4)(cod)]$ (1 mmol) and 252 mg of KTp are dissolved in ca. 40 mL of acetone, and the mixture is stirred at room temperature for 1 h. The solvent is removed under reduced pressure and the oily residue dissolved in 30 mL of CH_2Cl_2. The colorless solution is cooled to −80 °C and ca. 150 mL of NO_2 bubbled through, turning the solution dark yellow. The solvent is evaporated and the solid residue extracted with Et_2O. Product **5a** is obtained, after cooling to −30 °C, as a white microcrystalline solid by concentrating this solution. Yield: 40%. Anal. Calcd for $C_{19}H_{22}BN_7O_2$-Pd: C, 45.86; H, 4.46; N, 19.70. Found: C, 45.76; H, 4.32; N, 19.57. IR (Nujol): $\nu(B-H)$ 2518 cm^{-1}, $\nu(NO_2)$ 1445 and 1326 cm^{-1}.