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Inorganica Chimica Acta 240 (1995) 299–304

Inorganica Chimica Acta

Palladium complexes present during the catalytic reduction of NO to N_2O ☆

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Received 20 January 1995; revised 28 April 1995

Abstract

The identity of a palladium chloronitrosyl complex, active in the catalytic reduction of NO to N_2O, has been examined in aqueous and non-aqueous media. Stoichiometry experiments for its formation from $[PdCl_4]^{2-}$ show the presence of one bound nitrosyl group per palladium and the requirement of a one-electron reductant, provided by CuCl. Work in non-aqueous solvents identified $[Pd_2Cl_4(NO)_2]^{2-}$ as a key intermediate, although in aqueous 2 M HCl the monomeric form $[PdCl_3(NO)]^{2-}$ is suggested to predominate, according to the equilibrium: $[Pd_2Cl_4(NO)_2]^{2-} + 2Cl^- \rightleftharpoons 2[PdCl_3(NO)]^{2-}$. The $[Ph_4As]_2[Pd_2Cl_4(NO)_2]$ complex could be oxidized to the stable compound $[Ph_4As]_2[Pd_2Cl_4(NO_2)_2]$, whose structure was determined by single crystal X-ray diffraction.

Keywords: Catalytic reduction; Palladium complexes; Nitrosyl complexes; Crystal structures

1. Introduction

Increasing awareness of the deleterious environmental impact of nitrogen oxides has sparked a resurgence in the study of their fundamental chemistry. Stringent emission restrictions have spurred research on NO_x reduction to non-toxic N_2O and/or N_2. Even the partitioning between these two reduced compounds is important, because the long-lived nitrous oxide molecule has a resident atmospheric lifetime of about 150 years [1]. It is a greenhouse gas 270 times as effective [2] as CO_2 and it has been implicated in stratospheric ozone depletion processes [3]. Nitrous oxide is also an important byproduct of microbial respiration, being generated by both nitrification ($NH_4^+ \rightarrow NO_3^-$) and denitrification ($NO_3^- \rightarrow NO, N_2O, N_2$) pathways [4]. The combined action of terrestrial and oceanic bacteria represent the dominant source term in the global nitrous oxide budget [5]. Stratospheric nitrous oxide concentrations have been observed to be increasing at a rate of 0.3% per year [6]. Neither biotic nor anthropogenic sources of N_2O have been sufficiently well characterized to account for these increases [6], adding extra importance to the fundamental research on mechanisms for N_2O formation.

Palladium has been used extensively to facilitate the reduction of NO_x. Studies of heterogeneous Pd chemistry with nitrogen oxides have included the three-way (Pt/Pd/Rh) automotive catalyst [7], pure Pd metal surfaces [8], and palladium supported on zeolites and other high surface area materials [9]. Less attention has been devoted to exploring its homogeneous reactivity.

Kubota et al. have described the reduction of NO to N_2O by CO, which was postulated to proceed by a Wacker-type mechanism catalyzed by $PdCl_2$ and $CuCl_2$ in 2 M HCl [10]. As part of an ongoing investigation of the mechanisms for nitrous oxide formation, we have further explored the identity of a spectroscopic intermediate observed, but never fully characterized. This paper describes the coordination chemistry and general reactivity of palladium nitrosyl complexes in both aqueous and non-aqueous solvents.

2. Experimental

Except where otherwise noted, all reactions were performed under nitrogen with the use of standard Schlenk techniques. The handling and transfer of oxygen-sensitive solids was conducted in a Vacuum Atmospheres glovebox equipped with a Dri-train. UV–Vis spectra were recorded on a HP 8452A diode array spectrometer using 1.0 cm quartz cells. IR data were acquired with a Nicolet 510 FT-IR spectrometer

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☆ This paper is dedicated to Professor Fred Basolo on the occasion of his 75th birthday.

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SSDI 0020-1693(95)04546-L

with a MCT liquid-nitrogen-cooled detector. Solid-state spectra were collected as KBr pellets; liquid spectra were sampled in cells with CaF_2 windows and pathlengths of 0.05 or 0.2 mm. Gas-phase spectra were recorded in 10 cm pathlength cells with CaF_2 windows. A quartz UV chamber was incorporated into one of the gas-phase IR cells to permit direct correlation between UV spectral changes and the composition of the headspace gases. X-ray diffraction data were collected on a Siemens R3m/V diffractometer. Elemental analyses were conducted by Desert Analytics, Tucson, AZ.

Pd metal, $PdCl_2$, $[Ph_4As]Cl$, $[(n\text{-}Bu)_4N]Cl$, D_2O and DCl were commercially supplied, and were used as received. Cylinders of CO (Linde, 99% min. purity) and NO (Liquid Air, 99% min. purity) were used as gas sources; the NO was spectroscopically free of higher nitrogen oxides. CuCl was prepared according to the published procedure [11]. Aqueous solutions were prepared with HPLC-grade water, dichloromethane was distilled from CaH_2 and stored over molecular sieves, and methanol was distilled from Mg/I_2.

2.1. Preparation of $[Ph_4As]_2[Pd_2Cl_6]$

A solution containing 0.192 g (1.09 mmol) of $PdCl_2$ in 15 ml of 2 M HCl was prepared, and then treated dropwise with 5 ml of a 0.44 M solution of $[Ph_4As]Cl$ (2.2 mmol) dissolved in 2 M HCl. A precipitate formed immediately. The solution was stirred for 20 min; then the solids were collected on a fritted glass filter and dried under vacuum. The solid was redissolved in CH_2Cl_2 and layered with hexane, from which orange single-crystals were obtained. These crystals were used in the structure determination. Solution and KBr IR spectra of the material were very similar to those of $[Ph_4As]Cl$, with no additional peaks in the region 1000–4000 cm^{-1}. The UV–Vis spectrum of a CH_2Cl_2 solution showed an asymmetric band, with a maximum near 440 nm and a broad unresolved shoulder near 500 nm.

2.2. Preparation of $[Ph_4As]_2[Pd_2Cl_4(NO)_2]$ and $[Ph_4As]_2[Pd_2Cl_6]$ mixed crystals

A solution of 0.102 g (0.58 mmol) of $PdCl_2$ was prepared in 30 ml of 2 M HCl and stirred under an atmosphere of CO for 90 min to produce a finely divided black precipitate, at which time 0.62 g (1.4 mmol) of $[Ph_4As]Cl$ were added and dissolved. The atmosphere of CO was removed under vacuum, replaced with an atmosphere of NO, and stirred for 1 h. The resulting solid was collected on a fritted glass filter. This brown precipitate dissolved in CH_2Cl_2 to produce an intense green–blue solution with an absorbance maximum at 582 nm.

IR spectra recorded in CH_2Cl_2 solution revealed ν_{NO} at 1701 and 1623 cm^{-1}. Solid-phase KBr pellet IR spectra showed a ν_{NO} at 1651 cm^{-1} with poorly defined shoulders at lower frequency. This is in good agreement with a previous report of ν_{NO} at 1623 cm^{-1} for $[TPBP]_2[Pd_2Cl_4(NO)_2]$ [12].

$[(n\text{-}Bu)_4N]_2[Pd_2Cl_4(NO)_2]$ could also be prepared by the reaction between Pd(0) and NO in a dichloromethane solution containing $[(n\text{-}Bu)_4N]Cl$. ν_{NO} at 1654 cm^{-1} was observed for the isolated solid.

Elemental analyses were performed on the bulk crystals isolated from CH_2Cl_2/hexane solution, which indicated a ratio of approximately 43% $[Ph_4As]_2[Pd_2Cl_4(NO)_2]$ and 57% $[Ph_4As]_2[Pd_2Cl_6]$. Two different X-ray diffraction data sets were collected, one at room temperature and one at −96 C°, but in neither instance was it possible to resolve the positions of the nitrosyl groups. The unit cell parameters for the mixed crystals were indistinguishable from those of pure $[Ph_4As]_2[Pd_2Cl_6]$.

2.3. Preparation of $[Ph_4As]_2[Pd_2Cl_4(NO_2)_2]$

Air oxidation of CH_2Cl_2 solutions of $[Ph_4As]_2[Pd_2Cl_4(NO)_2]$ resulted in the quantitative formation of $[Ph_4As]_2[Pd_2Cl_4(NO_2)_2]$, which could be crystallized from layered CH_2Cl_2/hexane solutions. Difference IR spectra showed loss of the ν_{NO} absorbances at 1701 and 1623 cm^{-1}, with the concomitant appearance of new peaks (1439, 1324 and 824 cm^{-1}) for N-bound nitro ligands, consistent with a previous synthesis of this material (ν_{NO_2}: 1407, 1320 cm^{-1}, δ_{NO_2}: 820 cm^{-1}) [12]. UV–Vis spectra recorded during the reaction showed two isosbestic points during the conversion between the two species. The UV–Vis spectrum of $[Ph_4As]_2[Pd_2Cl_4(NO_2)_2]$ in dichloromethane consists of a symmetric peak with a maximum at 430 nm.

2.4. X-ray crystallography

Single-crystal X-ray diffraction data were collected for $[Ph_4As]_2[Pd_2Cl_6]$ and $[Ph_4As]_2[Pd_2Cl_4(NO_2)_2]$. The data were collected at room temperature on a Siemens R3m/V diffractometer, over a 2θ range $3 < 2\theta < 50°$, using a Wyckoff scan. Structures were solved with direct methods and refined using a full-matrix least-squares procedure with SHELXTL PLUS software. $[Ph_4As]_2[Pd_2Cl_6]$ was refined with 234 parameters on 3383 observed ($F > 4.0\sigma F$) reflections to $R = 3.15\%$, $R_w = 4.65\%$, $GOF = 1.15$. $[Ph_4As]_2[Pd_2Cl_4(NO_2)_2]$ was refined with 216 parameters on 3445 observed ($F > 4.0\sigma F$) reflections to $R = 3.48\%$, $R_w = 5.01\%$, $GOF = 1.25$.

2.5. Determining the Cu:Pd stoichiometry of the initially formed palladium catalyst

In each of three sets of experiments, 4.0 ml aliquots from a 2 M HCl solution of CuCl (0.10 M) and $PdCl_2$ were reacted with NO for short periods of time. Concentrations of the $PdCl_2$ solutions used were 3.2×10^{-3}, 5.0×10^{-3} and 8.2×10^{-3} M, respectively. Each reaction was quenched by quickly pumping away the atmosphere of NO and replacing it with N_2. The amount of Cu^{2+} formed during the reaction was assayed by treating the sample with conc. NH_4OH and

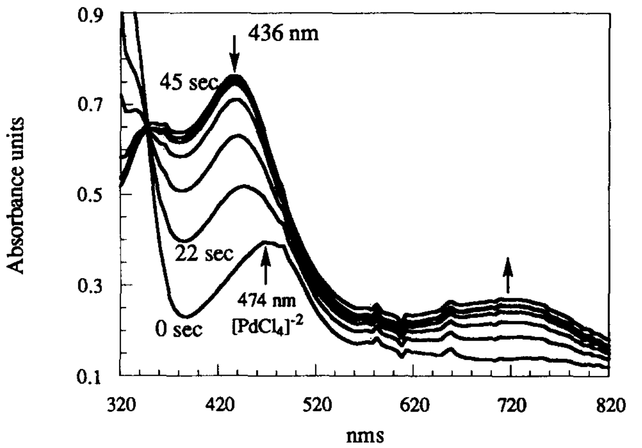

Fig. 1. UV–Vis spectral changes for the first 45 s during the formation of the catalytically active complex from 3.1×10^{-3} M $[PdCl_4]^{2-}$, 800 torr NO, and 0.1 M CuCl in 2 M HCl.

determining the concentration of $[Cu(NH_3)_4]^{2+}$ spectrophotometrically. These values were corrected by blanks not exposed to NO. Complete conversion to the intermediate was determined from a plot of moles of Cu^{2+} produced versus reaction time. The ratio of moles of Cu^{2+} generated to moles of Pd^{2+} in the solution was 1.1(±0.1):1 for the three trials.

2.6. Determining the NO:Pd stoichiometry of the initially formed palladium catalyst

A gas burette was introduced into the reaction apparatus such that a fixed volume of NO at atmospheric pressure could be reacted with 20 ml of solution. A bulk solution of 0.10 M CuCl in 2 M HCl was prepared, and blank runs were conducted to measure the uptake of NO into the solution in the absence of $PdCl_2$. Equilibrium was established quickly, and the measured NO solubility of 1.0×10^{-3} M was in very good agreement with literature values [13].

Two separate solutions of $PdCl_2$ (5.7×10^{-3} M and 5.3×10^{-3} M) were prepared from the bulk CuCl solution used for the blanks. Three trials were run for each solution. After correcting for the quantity of NO unreacted in solution, the results of these experiments were consistently low, with an NO:$PdCl_2$ ratio of 0.69(±0.04):1. Estimates for the amount of N_2O being reintroduced back into the headspace, determined from the Henry's Law constant for N_2O and its rate of formation measured at the same reagent concentrations in separate experiments, corrected this value to about 0.8:1.

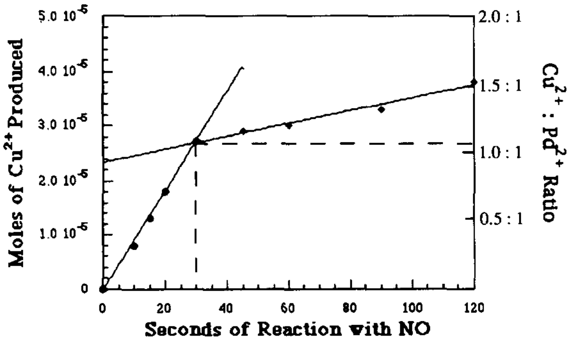

Fig. 2. Plot of Cu^{2+} generated vs. time; 2 M HCl, $[PdCl_4]^{2-}=5.0\times10^{-3}$ M, [CuCl] = 0.10 M, total moles of $Pd^{2+}=2.5\times10^{-5}$.

3. Results and discussion

In the initial paper of Kubota et al., a UV–Vis spectroscopic intermediate was observed to form at 450 nm during the catalytic reduction of NO to N_2O. It was postulated that this intermediate might be a complex incorporating NO, $PdCl_2$ and CuCl [10]. In our hands, the addition of NO to a solution of $[PdCl_4]^{2-}$ and CuCl in 2 M HCl causes the band at 474 nm assigned to the tetrachloropalladium anion to blue-shift to 434 nm, with concomitant doubling of the observed absorption intensity. During formation of the intermediate the single absorption maximum varied along a continuum between 434 and 474 nm (Fig. 1). This behavior probably results from overlapping of the closely spaced absorbances of the catalytic species and $[PdCl_4]^{2-}$.

No reaction occurred between $[PdCl_4]^{2-}$ and NO when CuCl was omitted, or when $CuCl_2$ was used instead. In reactions where CuCl was initially present, Cu^{2+} was observed to form at the same time as the band at 434 was generated. This suggests that a reducing agent is essential in the reaction of nitric oxide with $[PdCl_4]^{2-}$.

Reduction of $[PdCl_4]^{2-}$ with CO in 2 M HCl produced a finely divided black precipitate, which when stirred with an atmosphere of NO generated the same spectroscopic intermediate at 434 nm in the absence of cuprous chloride. Similar results were obtained by directly reacting Pd metal powder and NO in 2 M HCl, showing that CuCl is not required for formation of the catalytic intermediate. For solutions prepared in this manner, the 434 nm absorption slowly red-shifted back to 474 nm, while N_2O appeared in the headspace gases of the UV–Vis IR cell.

A series of reactivity studies was undertaken to determine how much Cu^+ is oxidized to Cu^{2+} during formation of the N_2O-generating species. Fig. 2 shows a plot of the quantity of Cu^{2+} generated as a function of time. The steep initial slope arises from the rapid formation of the nitrosyl palladium species, while the slower rate of formation at later times arises from the catalytic cycling of NO to N_2O by a steady-state concentration of the active catalytic intermediate. Because the rate of formation of the intermediate is about an order of magnitude faster than its subsequent reactions, its steady-state concentration was assumed to be the same as the initial concentration of $PdCl_2$. Extrapolating the two limiting rates to a common point of intersection allowed an estimate of the time required to completely form the intermediate. For the two trials at low $PdCl_2$ concentrations (3.2×10^{-3} and 5.0×10^{-3} M) the conversion time was 30±1 s, and the ratio of Cu^{2+} formed to $PdCl_2$ present was 1.1:1 in each trial. At a $PdCl_2$ concentration of 8.2×10^{-3} M, the time required to reach full conversion was longer and the break point was less well defined. This was attributed to rate-limiting diffusion of NO into solution. The Cu^{2+}:$PdCl_2$ ratio was 1.2:1 in this trial, consistent with additional catalytic cycling occurring during the longer time required to completely form the initial catalyst.

Measurement of the rate of uptake of NO during this period was complicated by the short time frame involved and the problems of catalytic turnover reevolving gaseous products, but even with these corrections the ratio of nitric oxide to palladium was near 1:1. Both the Cu^+ and NO stoichiometry argue for a mononitrosyl complex as the initial palladium species.

Based on the stoichiometry observations above, the formation of the spectroscopic intermediate observed under aqueous catalytic conditions can be written as Eq. (1).

$$[PdCl_4]^{2-} + NO + Cu^+ \rightarrow [PdCl_3(NO)]^{2-} + Cl^- + Cu^{2+} \quad (1)$$

This overall reaction can be postulated to proceed in two elementary steps (Eqs. (2) and (3)), beginning with the initial exchange of a chloride ligand for a nitrosyl group. This would require an odd formal oxidation state for the palladium (+1 or +3, based on assignment of $(NO)^+$ or $(NO)^-$ to the nitrosyl ligand). The presence of Cu^+ could provide an electron to the intermediate, stabilizing it as $[PdCl_3(NO)]^{2-}$.

$$[PdCl_4]^{2-} + NO \rightleftharpoons \{PdCl_3(NO)^-\} + Cl^- \quad (2)$$

$$\{PdCl_3(NO)^-\} + Cu^+ \rightarrow [PdCl_3(NO)]^{2-} + Cu^{2+} \quad (3)$$

An alternative explanation for the role of the copper would involve initial formation of a copper nitrosyl complex, which then serves as a transfer agent to exchange NO^- directly for a chloride ligand.

$$CuCl + NO \rightleftharpoons Cu(NO)Cl \quad (4)$$

$$[PdCl_4]^{2-} + Cu(NO)Cl \rightarrow [PdCl_3(NO)]^{2-} + CuCl_2 \quad (5)$$

CuCl has previously been shown to fulfill an analogous role as a carbonyl transfer agent in the reduction of nitric oxide by carbon monoxide in the presence of platinum(II), copper(I) and copper(II) [14] and it is known to slowly reduce NO to N_2O even in the absence of palladium [15]. Experiments to differentiate between the two possible roles of action for the copper-mediated reduction are in progress.

Solution-phase IR spectra of the intermediate were recorded in 2 M HCl and in 2 M DCl/D_2O in an attempt to observe direct evidence for a palladium mononitrosyl complex, but the very limited throughput in the region of interest rendered these studies inconclusive. Consequently, the chemistry and spectroscopy of palladium nitrosyl complexes were investigated in non-aqueous solvents with the hope of extracting data that could be extrapolated to the aqueous results.

The known [12] anionic palladium complexes $[Pd_2Cl_6]^{2-}$, $[Pd_2Cl_4(NO)_2]^{2-}$ and $[Pd_2Cl_4(NO_2)_2]^{2-}$ were isolated (see Section 2) as $[Ph_4As]^+$ salts from CH_2Cl_2 solutions under conditions relevant to the non-aqueous catalyst system. Crystal structures of $[Ph_4As]_2[Pd_2Cl_6]$ and $[Ph_4As]_2[Pd_2Cl_4(NO_2)_2]$ were solved as part of the characterization of these compounds. The structure of the $[Pd_2Cl_6]^{2-}$ dianion has previously been reported [16], and it is in excellent agreement with the current data in all respects. The unit cell of $[Ph_4As]_2[Pd_2Cl_4(NO_2)_2]$ was found to be only marginally distorted from that of its hexachloro analog. Early refinements identified the sites of two N-bound nitro ligands related by a center of symmetry in the center of the dimeric unit. No disorder in the positioning was encountered. The oxygen atoms were positioned above and below the plane of the Pd_2Cl_6 unit (Fig. 3), with N–O bond lengths of 1.164(7) and 1.049(6) Å. Further structural features of the two compounds were unexceptional and do not merit further comment. Tables 1 and 2 contain the unit cells, fractional coordinates and isotropic displacement coefficients for the non-hydrogen atoms of $[Ph_4As]_2[Pd_2Cl_6]$ and $[Ph_4As]_2[Pd_2Cl_4(NO_2)_2]$, respectively. See also Section 5.

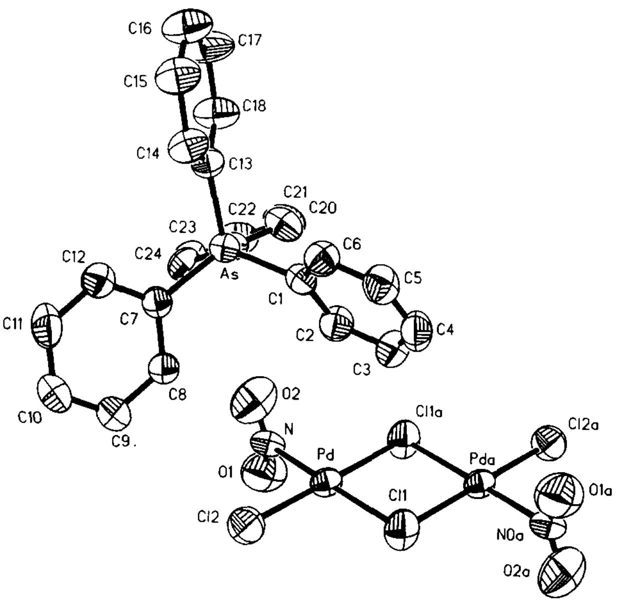

Fig. 3. Thermal ellipsoid plot showing the molecular structure of $[Ph_4As]_2[Pd_2Cl_4(NO_2)_2]$.

The relative instability of $[Ph_4As]_2[Pd_2Cl_4(NO)_2]$ toward loss of NO prevented successful crystallization of this material, which instead co-crystallized with $[Ph_4As]_2[Pd_2Cl_6]$, as determined by comparison of its IR and UV–Vis spectra with previous literature reports [12]. Further evidence for the structure of the dinuclear nitrosyl was its clean oxidation to $[Ph_4As]_2[Pd_2Cl_4(NO_2)_2]$ on exposing the solution to air. The latter species was characterized by X-ray crystallography (Fig. 3). Oxidation of coordinated nitrosyl to a nitro ligand with dioxygen is a well known reaction, studied mechanistically by Clarkson and Basolo [17].

Table 1
X-ray data for the structure of $[Ph_4As]_2[Pd_2Cl_6]$ [a]: atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$)

	x	y	z	U_{eq} [b]
Pd	4934(1)	210(1)	3462(1)	48(1)
Cl(1)	4600(2)	−1406(1)	5225(1)	70(1)
Cl(2)	4442(1)	−1003(1)	2296(1)	69(1)
Cl(3)	5236(2)	1850(1)	1814(1)	80(1)
As	341(1)	3371(1)	2627(1)	38(1)
C(2)	1565(2)	2018(3)	4547(3)	53(2)
C(3)	1580	1226	5697	57(2)
C(4)	391	766	6517	56(2)
C(5)	−813	1098	6187	56(2)
C(6)	−828	1890	5038	49(2)
C(1)	361	2350	4218	41(2)
C(8)	1980(3)	1481(3)	1161(3)	49(2)
C(9)	2370	719	196	60(2)
C(10)	1570	821	−609	69(2)
C(11)	381	1685	−449	72(3)
C(12)	−9	2447	516	57(2)
C(7)	790	2346	1321	41(2)
C(14)	−2533(3)	3771(2)	2941(3)	50(2)
C(15)	−3814	4494	3131	61(2)
C(16)	−3962	5782	3179	72(2)
C(17)	−2829	6347	3037	83(3)
C(18)	−1548	5623	2847	63(2)
C(13)	−1400	4335	2799	42(2)
C(20)	1813(3)	5108(3)	3050(2)	58(2)
C(21)	2698	6011	2659	69(2)
C(22)	3422	6295	1357	70(3)
C(23)	3261	5675	448	66(2)
C(24)	2375	4771	839	53(2)
C(19)	1651	4488	2141	43(2)

[a] Space group $P\bar{1}$, $a = 10.516(6)$, $b = 10.925(4)$, $c = 11.120(7)$ Å, $\alpha = 78.40(4)$, $\beta = 70.50(4)$, $\gamma = 78.76(4)$°.

[b] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Of particular importance was the identification of $[Pd_2Cl_4(NO)_2]^{2-}$ in precipitates directly isolated from aqueous solutions catalytically active in the reduction of NO. This was accomplished by dissolving $[PdCl_4]^{2-}$ and only a slight excess of CuCl in 2 M HCl, then reacting the solution with NO for 3 to 5 min. Adding $[Ph_4As]Cl$ at this point resulted in the formation of a brown precipitate and an almost complete loss of color from the solution. The solid material was not analytically pure. IR samples of the initial precipitate in KBr showed a broad asymmetric stretch at 1650 cm^{-1} with an unresolved shoulder on the low frequency side, characteristic of $[Ph_4As]_2[Pd_2Cl_4(NO)_2]$ [12]. When the precipitate was left as a thick wet paste, this IR stretch in the nitrosyl region disappeared within 12 to 24 h. IR monitoring of the headspace gases showed increasing concentrations of NO, N_2O and NO_2 during this time.

The isolation of an analytically pure palladium complex under catalytic conditions proved difficult for several reasons. CuCl is present in 2 M HCl as the complex anion $[CuCl_2]^-$ and coprecipitates on addition of a bulky cation. Furthermore, the constant catalytic turnover of the intermediate continually regenerates $[PdCl_4]^{2-}$, which is also precipitated from solution by $[Ph_4As]^+$. Drying the precipitate under vacuum in a chloride-rich environment tends to slowly deplete the nitrosyl IR stretch. However, the complex remains catalytically active when left wet, also depleting the nitrosyl stretch.

The tendency of palladium to form dinuclear species in non-aqueous systems and with large counterions is well established, thus the dinuclear complexes obtained from CH_2Cl_2 are not unexpected. It was observed early in these experiments that the active catalytic species could be prepared directly from Pd(0) and NO in 2 M HCl. Thus it is significant that we isolated precipitates that showed IR features characteristic of $[Ph_4As]_2[Pd_2Cl_4(NO)_2]$ directly from aqueous reaction conditions. Although the UV–Vis spectra show no direct evidence for the dinuclear species in aqueous solutions, its precipitation with bulky counterions suggests that the equilibrium of Eq. (6) may occur.

$$[Pd_2Cl_4(NO)_2]^{2-} + 2Cl^- \rightleftharpoons 2[PdCl_3(NO)]^{2-} \qquad (6)$$

A dinitrosyl complex, $Pd(NO)_2Cl_2$, can be prepared by reacting $PdCl_2$ with NO saturated with methanol vapor. It

Table 2
X-ray data for the structure of $[Ph_4As]_2[Pd_2Cl_4(NO)_2]$ [a]: atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$)

	x	y	z	U_{eq} [b]
Pd	4987(1)	232(1)	3446(1)	44(1)
Cl(1)	4549(2)	−1392(1)	5211(1)	65(1)
Cl(2)	4496(1)	−888(1)	2172(1)	64(1)
As	288(1)	3420(1)	2670(1)	39(1)
C(2)	1548(2)	2025(3)	4558(3)	54(2)
C(3)	1569	1214	5695	61(2)
C(4)	382	751	6515	60(2)
C(5)	−828	1101	6196	57(2)
C(6)	−850	1912	5059	51(2)
C(1)	338	2374	4240	43(2)
C(8)	1845(3)	1571(3)	1203(3)	47(2)
C(9)	2215	817	233	58(2)
C(10)	1394	927	−554	70(3)
C(11)	204	1791	−370	75(3)
C(12)	−166	2545	600	57(2)
C(7)	655	2435	1386	42(2)
C(14)	−2559(3)	3820(2)	2986(4)	53(2)
C(15)	−3830	4560	3159	62(2)
C(16)	−3957	5851	3183	76(3)
C(17)	−2813	6402	3033	87(3)
C(18)	−1542	5663	2860	65(2)
C(13)	−1415	4372	2836	44(2)
C(20)	1793(3)	5152(3)	3094(3)	61(2)
C(21)	2715	6024	2695	75(3)
C(22)	3459	6275	1395	70(3)
C(23)	3282	5654	493	65(2)
C(24)	2360	4782	892	50(2)
C(19)	1616	4531	2192	42(2)
N	5415(4)	1668(3)	1949(4)	44(2)
O(2)	4622(5)	2377(5)	1853(5)	100(3)
O(1)	6574(6)	1642(4)	1479(5)	104(3)

[a] Space group $P\bar{1}$, $a = 10.505(6)$, $b = 10.990(4)$, $c = 11.131(7)$ Å, $\alpha = 78.19(5)$, $\beta = 71.92(5)$, $\gamma = 79.61(5)$°.

[b] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

exhibits ν_{NO} at 1838 and 1818 cm^{-1} in nujol [18]. Similar results have been obtained by reacting a methanol suspension of $PdCl_2$ with an atmosphere of NO (ν_{NO} = 1821 cm^{-1} in KBr). Isolation of solid material, either by cooling or by vacuum evaporation of the methanol solvent, resulted in the additional formation of a polymeric palladium species, $[Pd(NO)Cl]_n$ (1759 and 1715 cm^{-1} in KBr, versus literature values of 1764 and 1712 cm^{-1}) [19]. The decomposition of $Pd(NO)_2Cl_2$ into $[Pd(NO)Cl]_n$ has been reported in the literature [19], although neither the identity of other products nor the overall mechanism of the reaction was discussed.

We have determined that dissolving $Pd(NO)_2Cl_2$ and $[Pd(NO)Cl]_n$ in 2 M HCl generates a UV–Vis absorbing species at 440 nm that slowly shifts to 468 nm, concomitant with the generation of N_2O. This is consistent with the results of the aqueous chemistry discussed previously, for the formation of $[Pd_2Cl_4(NO)_2]^{2-}$ from $[Pd(NO)Cl]_n$ has been reported to occur [19] according to Eq. (7).

$$2[Pd(NO)Cl]_n + 2Cl^- \rightarrow [Pd_2Cl_4(NO)_2]^{2-} \quad (7)$$

Further support is provided by the observation that the addition of a 2-fold excess of $[Ph_4As]Cl$ to a methanolic solution of $Pd(NO)_2Cl_2$ resulted in rapid precipitation of a dark brown solid. A KBr spectrum of the material reveals an IR band at 1651 cm^{-1} with low-frequency shoulders. This material dissolves in dichloromethane, and its UV–Vis and IR spectra indicate that it is a mixture of $[Ph_4As]_2[Pd_2Cl_6]$ and $[Ph_4As]_2[Pd_2Cl_4(NO)_2]$.

It should be noted in closing that the data presented here run counter to earlier suggestions that the reduction of NO to N_2O by palladium complexes proceeds through formation of a hyponitrite moiety from *cis*-$Pd(NO)_2Cl_2$ [10,20]. Such a mechanism would be analogous with the chemistry of other metal dinitrosyls [21] and consistent with the structure identified in $[Pt(PPh_3)_2(N_2O_2)]$ [22]. Although a dinitrosylpalladium catalyst species could be present in small amounts, it is inconsistent with the stoichiometry and the major complexes present during catalysis.

4. Conclusions

The spectroscopic intermediate observed in the palladium-catalyzed reduction of NO to N_2O consists of an anionic chloropalladium species with a single bound nitrosyl ligand. A palladium:NO stoichiometry close to 1:1 has been determined. In contrast to previous hypotheses, the role of CuCl has been identified as being limited to that of a reductant or NO^- transfer agent. Dinuclear $[Pd_2Cl_4(NO)_2]^{2-}$ has been identified as the corresponding palladium nitrosyl complex generated in non-aqueous solvents, which is also active in N_2O formation. In aqueous solutions with excess chloride, the corresponding monomeric complex $[PdCl_3(NO)]^{2-}$ is proposed to be the major precursor to N_2O production. The absence of a dinitrosyl species suggests that N_2O formation may proceed by attack of NO(gas) on the palladium-bound NO group. Kinetic studies of the catalytic mechanism are in progress.

5. Supplementary material

Complete structural details, including unit-cell data, fractional coordinates, anisotropic temperature factors for non-hydrogen atoms and isotropic parameters for hydrogens have been deposited with the Cambridge Crystallographic Database.

Acknowledgements

We thank the National Science Foundation Grant No. CHE-9216618 for support of this research.

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