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Group 8 and 10 hyponitrite and dinitrosyl complexes

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Abstract

cis-Hyponitrite complexes $L_nM(N_2O_2)$ (M = Ni, Pt; $L_n = PPh_3$, PPh_2Me, dppe, and dppf) of divalent group 10 metals have been previously shown to be readily prepared by treating the corresponding L_nMCl_2 derivatives with sodium-(*Z*)-1-{4-(2,6-di-*tert*-butyl-4-meth-oxycyclohexadienonyl)}diazen-1-ium-1,2-diolate. These complexes adopt a diamagnetic square planar geometry with oxygen bound chelating planar *cis*-hyponitrite ligands. They are readily prepared at room temperature but thermally decompose above 90 °C with release of nitrous oxide. Electrophiles such as iodine, methyltriflate, and hydrochloric acid also react rapidly with the *cis*-hyponitrite complexes to give nitrous oxide. The structure of one of these previously prepared complexes, (PPh_3)₂Pt(N₂O₂), has been redetermined at -100 °C as a dichloromethane solvate with improved precision. The related tetrahedral group 8 dinitrosyl complexes, (PPh_3)₂M(NO)₂ (M = Ru, Os; $L_n = PPh_3$, dppe, and dppf) have been reexamined and new derivatives with chelating phosphines have been prepared by ligand substitution on the corresponding (PPh_3)₂M(NO)₂. The structures of Ru(dppf)(NO)₂ and Os(dppe)(NO)₂ have been determined. These two analogous families of *cis*-hyponitrite and dinitrosyl complexes illustrate the balance of metal dⁿ electron count and nitrosyl redox state with one having linear nitrosyls bound to low valent metal centers, and the former having coupled N₂O₂²⁻ ligands bound to a higher oxidation state metal center.

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1. Introduction

Perhaps one of the most striking differences between the organometallic chemistries of carbonyl and nitrosyl complexes is the remarkable prevalence of binary or homoleptic metallocarbonyls [1] and the absence of the related metallonitrosyls [2]. Thus although many homoleptic carbonyls with the general formula $M_y(CO)_x$ are known, only one nitrosyl analog, $Cr(NO)_4$, can be considered to be well characterized [3]. The evidence for the other proposed homoleptic nitrosyls such as $Fe(NO)_4$ and $Co(NO)_3$ is considerably less persuasive [4,5] and has recently been critically reappraised [2]. Given the well recognized isolobal relationship between the carbonyl and nitrosonium ligands, *a priori* there seems to be little theoretical basis to account

for this trend. Nevertheless, NO's amphoteric ability to bind as either a bent or linear ligand [6], as well as its ability to promote associative substitution reactions [7] complicates its coordination chemistry

$$NO + NO \rightleftharpoons [NO]_2 \tag{1}$$

$$3NO \rightarrow NO_2 + N_2O$$
 (2)

Certainly, an important factor which can explain the paucity of homoleptic metallonitrosyls is synthetic; many metallocarbonyls are prepared under reductive conditions with high pressures of carbon monoxide [8], conditions which are not suited to handling NO. Two important features of nitric oxide chemistry are likely to limit the utility of these direct approaches: (1) nitric oxide undergoes a kinetically important dimerization to give $[NO]_2$, **1** Eqs. (1); and (2) nitric oxide, and its dimer, readily disproportionate, Eq. (2). Moreover, NO and $[NO]_2$ can engage in redox chemistry either with low valent metals or with itself in

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the form of metal catalyzed disproportionation. And of course any disproportionation, metal catalyzed or not, leads to the formation of the very strongly oxidizing nitrogen dioxide. It is significant that the original syntheses of $Cr(NO)_4$ involves a photolytic substitution under a stream of nitric oxide at atmospheric pressure [3,9,10], conditions which favor the binding monomeric nitric oxide and not nitric oxide disproportionation or the reaction of the complex with the nitric oxide dimer.

In addition to these fundamental synthetic limitations there is an additional reactivity pattern possible for polynitrosyl complexes which is not observed for polycarbonyls: metal mediated nitric oxide coupling to give N–N bonded derivatives either as hyponitrite [11–14], or nitrous oxide [15] or in some cases ultimately to give dinitrogen [16]. Unfortunately, the evidence for the direct coupling of two nitrosyls in the coordination sphere of a metal is limited and a clear unambiguous example of the reaction in Eq. (3) would help us understand the nature of this transformation. The ambiguity present here is mechanistic: Are either of the nitrosyls coordinated to the metal before N–N bond formation, Eq. (3), or do these N–N coupled products result from the reaction of the dimer 1 with the metal, Eq. (4)?

$$L_n M(NO)_2 \longrightarrow L_n M(\eta^n - ON = NO)$$
 (3)

$$L_{n}M + [NO]_{2} \longrightarrow \qquad \begin{array}{c} L & O \\ M & \parallel \\ 0 \\ N \end{array}$$
(4)

Examples of metal mediated nitric oxide reductive coupling which give isolable hyponitrite complexes are rare and correspond to the nitrosylation of several electron rich late transition metal complexes, Eqs. (5)-(8) [12-14]. In the ruthenium and platinum examples the corresponding dinitrosyl complexes were not isolated, and have not been reported. The reaction of Pt(PPh₃)₄ with nitric oxide proceeds in a straightforward manner involving the reductive dimerization of nitric oxide to yield a cishyponitrite ligated Pt(II) complex (Eq. (5)) [12]. A more complicated reaction between Co(CO)₃(NO) and excess nitric oxide also proceeds via reductive dimerization of nitric oxide, Eq. (7). In this case the formation of the putative $[Co(NO)_3]$ intermediate is also proposed [13]. Finally, the example shown of the reductive coupling of two Co(II) nitrosyl complexes in Eq. (8), $\{CoNO\}^8$ in the Feltham-Enemark scheme [17], is a well studied [18-20] example known since Werner's pioneering chemistry [21]. In the absence of added reductants nitric oxide coupling can occur with metal oxidation [16] or by nitric oxide disproportionation, Eq. (2). Thus, the reductive nitric oxide coupling which occurs in Eqs. (5)–(8) are likely to be quite common and most likely related to the general metal catalyzed disproportionation of NO by transition metals [15,22] and more recently by lanthanides [23]. The current scarcity of hyponitrite complexes as products of reductive nitrosylation reactions is in part due to their

instability and in particular their tendency to lose nitrous oxide [24].



The facile loss of nitrous oxide from the cis-hyponitrite complex is one of its key reactivity patterns; it is also important for the uncoordinated ligand. We have attributed this to the instability of the monoalkyl or monoprotonated cis-hyponitrite. To demonstrate this point the contrast with *trans*-hyponitrite and its conjugate acid and esters is illustrative. Thus although a series of monoalkylated and protonated *trans*-hyponitrites are now recognized, these correspond to the kinetically activated form which releases nitrous oxide. Unlike trans-hyponitrite for which stable dialkylated and diprotonated derivatives can be isolated and characterized, neither is known for the *cis* isomer. We attribute this tendency to the instability of the monoprotonated and monoalkylated *cis*-hyponitrite: addition of the second electrophile can not compete with loss of nitrous oxide. This hypothesis accounts for the instability of *cis*-hyponitrite complexes: any coordination sphere lability which leads to a monohapto cis hyponitrite could rapidly lose nitrous oxide. A second consequence of this hypothesis is that the preparation of *cis*-hyponitrite complexes will most likely require prior coordination of the oxygens in the precursor or oxidative addition of the nitric oxide dimer, rather than by direct coordination of the preformed dianion. In this paper, we report: (1) the preparation and characteristics of *cis*-hyponitrite complexes; (2)

the redetermination of the structure of one of these, Pt(PPh₃)₂(N₂O₂), with a significantly improved precision; (3) the syntheses and characterization of new dinitrosyl complexes of ruthenium and osmium with chelating phosphines; and (4) the structures of two of these derivatives, Ru(dppf)(NO)₂ and Os(dppe)(NO)₂.

2. Results and discussion

Two streams of experimental data are contrasted in this paper: the stable group 10 M(II) hyponitrite complexes, 2, for which the corresponding dinitrosyls are not known, and the stable group 8 dinitrosyls, 3, for which stable mononuclear hyponitrite complexes have not been described



Fig. 1. ORTEP representation of the inner coordination sphere of **2a**. Probability elliposoids shown at 45% and key metric parameters (Å, °): O(1)–N(1) = 1.370(8); N(1)–N(2) = 1.230(9); N(2)–O(2) = 1.363(8); O(1)–Pt(1) = 2.013(4); O(2)–Pt(1) = 2.023(5); Pt(1)–P(1) = 2.2417(17); Pt(1)–P(2) = 2.2671(18) Å; Pt(1)–O(1)–N(1) = 112.1(4); O(1)–N(1)–N(2) = 118.9(7); N(1)–N(2)–O(2) = 118.5(7); N(2)–O(2)–Pt(1) = 112.3(5); O(1)–Pt(1)–O(2) = 78.2(2); O(1)–Pt(1)–P(1) = 93.23(15); O(1)–Pt(1)–P(2) = 168.56(15); O(2)–Pt(1)–P(1) = 171.40(15); O(2)–Pt(1)–P(2) = 90.79.15(15); P(1)–Pt(1)–P(2) = 97.80(7)°.

lar to the dianion in its sodium salt [25], but the latter structure is based on the Rietveld refinement of its powder data and the key anion bond lengths and angles have high esd's, cf. O(1)–N(1)=1.40(3); N(1)–N(2) = 1.20(3); N(2)–O(2) = 1.41(3) Å and N(2)–N(1)–O(1) = 120.8(4)°, N(1)–N(2)– O(2) = 117.6(4)° which limits their interpretation.



In prior work [24], we have termed the reaction in Eq. (9) an umpolung of the C–N bond: on a formal level the bond cleaves heterolytically to give $[N_2O_2]^{2-}$ rather than to generate two NO radicals as do many diazeniumdiolates [29]. The quinone by-product has been quantified and corresponds well to the yield of **2**. Typically, two equivalents of **4** are used for every metal complex, but when the stoichiometry is 1:1 the yield of **2a** is only slightly less than if two equivalents are used. In understanding this transformation the origin of the 4-oxygen of the quinone is crucial, but uncertain. On the one hand the diazeniumdiolate **4** seems

2.1. Coordinated hyponitrite

It remains remarkable how few cis-hyponitrite complexes there are and how poorly developed the chemistry of this ostensibly simple dianion remains: in part this reflects the extreme reactivity of its simple salts [24], of which the disodium salt was only thoroughly characterized in 1996 [25,26]. In contrast, there are many more reports related to *trans*-hyponitrite, it is easier to prepare and it has greater stability [27,28]. The first and until recently unique example of the mononuclear *cis*-hyponitrite complexes 2a with $L = PPh_3$ and M = Pt was first prepared by treating $Pt(PPh_3)_4$ with NO [11,12]. In 2002, we described a new way to prepare these derivatives by treating MCl_2L_2 , M = Ni, Pt, with the diazenium diolate 4, Eq. (9). In addition to the generality of the possible substrates for the generation of 2 their yields and purity are higher with this synthesis. Detailed spectroscopic and characteristic data are listed in Section 4, 2a-e, and the structure for 2a has been redetermined since the original had large esd's for the metric parameters for the hyponitrite ligand, and the modeled solution had a very high R factor, R > 10% [12]. Although these crystallographic problems limited the detailed interpretation of the structure of 2a it did confirm its composition. These limitations are due to the original data being acquired at room temperature, where there is considerable decomposition. Our redetermination corresponds to the -100 °C structure. A side on view of the inner coordination environment of 2a is shown in Fig. 1, and key metric parameters are included in the caption. The geometry adopted by the *cis*-hyponitrite in 2a is similar to that in Ni(dppf)(N_2O_2) [24] and the metric parameters are simito require the methyloxy substituent as its alkyl substituted relatives do not react as rapidly with acids to release nitrous oxide as readily as 4. This observation suggests that coordination of 4 might lead to its facile demethylation and that the oxygen is thus retained in the quinone. On the other hand, when the reaction in Eq. (9) is performed for Pt(PPh₃)₂Cl₂ with anhydrous solvents the yield drops from 72% to 11%. Thus a hydrolytic mechanism is implicated in Eq. (9). Curiously none of our numerous attempts to adapt this preparation to the related palladium complexes has returned isolable crystalline products or products with the key IR bands at circa 1260, 790 cm^{-1} . Regardless of the mechanistic details of these syntheses, the facile formation of new cis-hyponitrite complexes, and the first examples of their nickel complexes, allows for the systematic examination of their chemistry [24].



These group 10 square planar divalent hyponitrite complexes are sensitive to heat, light, acids, and oxidation. Their thermal decomposition has been monitored by differential scanning calorimetry and they typically decompose exothermally at T > 85 °C. To date the only well characterized products of these reactions are the oxide of the phosphine, nitrous oxide, and in the case of the platinum complexes, the colloidal metal. Phosphine oxide is also produced when the decomposition is done with strict exclusion of oxygen. This suggests that decomposition follows the stoichiometry in Eq. (10) where colloidal platinum metal results from the reductive formation of the phosphine oxide, after loss of nitrous oxide. The observed kinetics of nitrous oxide release and complex decomposition are both first order with the same rate constant, within experimental error [24]. The trapping of the oxo intermediate with carbon disulfide and carbon dioxide support its intermediacy [24], and we note that a stable terminal platinum oxide in a Pt(IV) complex has recently been reported [30]. What remains absent in all of the decomposition products of 2 are complexes with nitrosyl ligands as demonstrated by the absence of nitrosyl peaks in their IR spectra. There is no evidence that nitric oxide coupling is reversible in this system, nor is there evidence for stable nitrous oxide complexes in the products.

Based on the yield of $Pt(PPh_3)_2I_2$ and the observed formation of triphenylphosphine oxide, the stoichiometric equation was proposed to involve two moles of **2a** and one mole of iodine:

$$2Pt(PPh_3)_2(O_2N_2) + l_2 \rightarrow Pt(PPh_3)_2l_2 + 2N_2O + 2OPPh_3 + Pt(0)$$

When the reaction between 2a and iodine was monitored by ³¹P NMR with the proposed stoichiometry, the amount

of triphenylphosphine oxide formed was integrated against a triphenylphosphine sulfide standard, and the integrated ratio was identical to the calculated mole ratio.

The oxidative addition reactions of $Pt(PPh_3)_2(N_2O_2)$ with methyl iodide, methyl triflate, iodine, and hydrochloric acid have been examined to determine if it is possible to isolate a Pt(IV) complex with a hyponitrite ligand. With iodine as a solution in methylene chloride there is a rapid reaction which ensues at -78 °C and goes to completion as the reaction is warmed over an hour to give a bright yellow precipitate of *trans*-Pt(PPh₃)₂I₂. This same product forms only slowly and in low yield when 2a is treated with iodomethane under these conditions. In the later case even after 48 h most of the 2a has not reacted and is recovered from the reaction. In the latter case a peak for trans-Pt(PPh₃)₂(CH₃)I is not seen in the ³¹P NMR spectrum [31]. With methyltriflate a white precipitate of $[Pt(PPh_3)_2(\mu-OH)]_2[OSO_2CF_3]_2$ forms in 71% yield in the course of the warming the reaction mixture from -78 °C to room temperature.

2.2. Dinitrosyls

Although the dinitrosyls of group 8 metals were some of the first prepared, *cf.* Roussin's red and black salts of iron [32], the isolation of a ruthenium dinitrosyl complex, [RuCl(NO)₂(PPh₃)₂]BF₄, with both a bent and linear nitrosyl ligands remains an excellent example of the amphoteric nature of the nitrosyl ligand [6,33]. Perhaps equally remarkable is the reduced neutral analog, Ru(NO)₂(PPh₃)₂ which has two linear nitrosyls and remains one of the few isolable tetrahedral low valent ruthenium derivatives [34]. In spite of their early and facile preparation, Eq. (11), which has since been optimized [35], the chemistry of these derivatives remains surprisingly limited to reports of its oxygenation [34], oxidative addition [36–39], catalytic CO/NO metathesis [40–42], and electrochemistry [43].



Although nitric oxide exchange is reported to be fast for 3a [44], attempts to prepare pyridine, 2,2'-bipyridine, and 1,10-phenanthroline complexes by ligand exchange with the triphenylphosphine failed to generate new nitrogen

base analogs of 3a [35]. The inability of nitrogen based donors, even chelating donors, to substitute for triphenylphosphine is not surprising given that many low oxidation state osmium complexes are known for phosphines but few for ammines. We hypothesized that a chelating phosphine could substitute for the two triphenylphosphine in 3a,b and demonstrated this with the facile preparation of the bisdiphenylphosphinoferrocene complex of ruthenium 3c, and the diphenylphosphinoethane complex of osmium 3d, Eq. (12). Both of these substitution reactions have to be carried out in the strict exclusion of oxygen, but the products form in high yield and are readily isolated by recrystallization of the reaction mixtures. All of the dinitrosyl complexes 3 are a red-brown color which is due to a long tailing UV band which has considerable extinction in the visible. In the process of characterizing the UV-Vis activity of 3c,d a slow oxygen independent photochemical decomposition process was discovered. Nevertheless, 3d in particular is very reactive towards oxygen in solution or as a solid and rapidly decomposes within 20 min of exposure to oxygen. This is in contrast to the behavior of **3a,d** which decompose much more slowly and are readily purified by recrystallization in the open. As was found for 3b the product of the reaction of oxygen and 3d is a mononitrosyl with a coordinated nitrate [34]. There is no precedence in this system for nitrosyl coupling to give a stable or intermediary hyponitrite ligand analogous to 2.

To understand the structure and reactivity of **3c,d** both complexes have been characterized by single crystal X-ray diffraction. ORTEP representations for both are depicted in Figs. 2 and 3, with representative bond lengths listed



Fig. 2. ORTEP representation of **3c** at 30% probability level and hydrogens omitted. Key metric parameters: Ru(1)-P(1) = 2.3478(14), Ru(1)-P(2) = 2.3667(13), Ru(1)-N(1) = 1.762(5), Ru(1)-N(2) = 1.781(4) Å; N(1)-Ru(1)-N(2) = 132.1(2), P(1)-Ru(1)-P(2) = 101.80(5), P(1)-Ru(1)-N(1) 97.2(2), P(1)-Ru(1)-N(2) 108.98(16), P(2)-Ru(1)-N(1) = 111.50(18), and $P(2)-Ru(1)-N(2) = 101.729(16)^{\circ}$.



Fig. 3. ORTEP representation of **3d** at 30% probability level and hydrogens omitted. Key metric parameters: Os(1)-P(1) = 2.3143(15), Os(1)-P(2) = 2.3210(14), Os(1)-N(1) = 1.782(5), Os(1)-N(2) = 1.783(4) Å; N(1)-Os(1)-N(2) = 138.7(2), P(1)-Os(1)-P(2) = 84.30(5), P(1)-Os(1)-N(1) = 8.80(16), P(1)-Os(1)-N(2) = 109.98(19), P(2)-Os(1)-N(1) = 107.42(17), and $P(2)-Os(1)-N(2) = 104.42(17)^{\circ}$.

in the captions. As with $M(NO)_2(PPh_3)_2$ which have been characterized for M = Os [45] and Ru [46,47] both structures have a distorted tetrahedral geometry at the metal with the angle separating the two nitrosyl ligands being substantially larger, ca 139° as compared to the angle between the two phosphorus atoms which are 101.8° and 84.3° in 3c and 3d, respectively. Although the angle between the nitrosyl ligands is very similar to those found for the bistriphenylphosphine complexes, 139.2° and 139.1°, the chelating phosphines in 3c and 3d in these structure reduces the angle between the phosphorus atoms from 103.9° and 103.5° for **3a,b**, respectively to 84.3° in **3d**. This change in structure is also reflected in the nitrosyl stretching bands for **3c,d**, which are separated by slightly greater energies than in **3a,b**. It is difficult to attribute the increased reactivity of 3d with dioxygen to any one particular structural change found by crystallography. In general alkyl phosphines are better donor ligands than their corresponding aryl phosphine analogs. Therefore the increased sensitivity of 3d to dioxygen may be simply due to increased electron density on the metal from the better donor phosphine.

3. Conclusions

While the amphoteric coordination character of nitric oxide, with its concomitant ability to bind in bent and linear geometries, is well known, another potential manifestation of its redox balance with transition metals is its ability to couple to give a hyponitrite complex such as the five examples described in this paper. But does the coordinative reductive coupling of nitric oxide represent a real reactivity pattern or mechanism? Among the ways to answer this question would be with examples of the formation of a nitrosyl complex from hyponitrite, or alternatively, the formation of hyponitrite complex from a dinitrosyl complex. At this time there are no unambiguous examples of either reaction: the predominant reaction of hyponitrite complexes is elimination of nitrous oxide, and polynitrosyl complexes are not necessarily precursors to hyponitrites. An important origin for this mechanistic uncertainty is nitric oxide's ability to dimerize and thus, as with many of nitric oxides reactions, one of the key questions remains does nitric oxide react as the monomer or dimer? Moreover, is the absence of stable homoleptic polynitrosyls in part due to their tendency to undergo reductive coupling as the first step in an oxidative decomposition pathway? Until we have clear evidence for the presence of these metal bound intermediates in these reactions, this hypothesis remains suggestive.

4. Experimental

4.1. General

The reagents and solvents used were reagent grade and used as supplied. Nitric oxide gas was obtained from Scott Specialty Gases and was purified by passing through a column packed with sodium hydroxide pellets. The nitrosylation apparatus and instrumental methods for these experiments are as described in prior publications [48,49]. Reagents were purchased from Aldrich and used as provided or purified as described in prior reports. Specific precursors were prepared by the literature methods including PtCl₂(PR₃)₂ [50,51], Ni(dppe)Cl₂ [52], Pt(dppf)Cl₂ [53], Ni(dppf)Cl₂ [52], Ru(NO)₂(PPh₃)₂ [54,34], and Os(NO)₂-(PPh₃)₂ [34], Ni(N₂O₂)(dppf) [24], sodium-(*Z*)-1-{4-(2,6-di*tert*-butyl-4-methoxycyclohexadienonyl)}diazen-1-ium-1,2-diolate [49], **4**, and sodium-(*Z*)-1-{4-(2,6-di*tert*-butyl-4-methoyleyclohexadienonyl)}diazen-1-ium-1,2-diolate (**6**) [49].

4.2. Preparation of complexes

4.2.1. $Pt(PPh_3)_2(N_2O_2)$ (2a)

Pt(PPh₃)₂Cl₂ (0.221 g, 0.280 mmol) is dissolved in 20 mL of acetonitrile/methylene chloride (1:1) and sodium-(Z)-1-{4-(2,6-di-*tert*-butyl-4-methoxycyclohexadienonyl)}diazen-1-ium-1,2-diolate (0.196 g, 0.616 mmol), **4**, dissolved in 25 mL of methanol, is added with constant stirring. The solution immediately turns yellow, and the mixture is allowed to stir for 5 min before all solvents are removed in vacuo. The resulting brownish solid material is taken up in 30 mL methylene chloride and allowed to stand for 10 min and filtered to remove any insoluble materials. Ethanol, 30 mL is then added, and solution volume concentrated to roughly half its volume and crystallization induced. Further concentration to 5 mL followed by filtration and successive washes with 5 mL each of ethanol,

ether, and hexanes gives 0.158 g, 72.4% of **2a**. DSC: $T_{\text{onset}} = 86.9 \text{ °C}$, $T_{\text{max}} = 103.8 \text{ °C}$, $\Delta H = 68.1 \text{ cal/g}$ (53.1 kcal/mole). IR (KBr, cm⁻¹): 1263 m, 1001 sh, 900.7 m, 793.7 m, 502.4 s.

UV–Vis (CH₂Cl₂, λ_{max} , nm (ε , M⁻¹ cm⁻¹)): 238 (28674). ¹H NMR (CD₂Cl₂, 400 MHz) δ 7.20 (t, 12H), 7.32–7.40 (m, 18H); ¹³C NMR (CD₂Cl₂, 400 MHz) δ 134, 131, 129, 128. ³¹P NMR (CD₂Cl₂, 400 MHz) δ 11.0 (¹J_{PtP} = 3564 Hz). The literature method [11] for the preparation of **2a** involves treating Pt(PPh₃)₄ with NO in benzene followed by recrystallization. In addition to **2a** a variety of other products appear to be formed and in our hands the synthesis above gives a higher yield of pure *cis*-hyponitrite complex.

4.2.2. $Pt(PPh_2Me)_2(N_2O_2)$ (2b)

Pt(PPh₂Me)₂Cl₂ (0.3775 g, 0.566 mmol), and **4**, 0.441 g, 1.34 mmol of are treated as for **2a**, to give 0.254 g, 68.4% **2b** as yellow crystals. *Anal*. Calc. for PtP₂C₂₆H₂₆N₂O₂: C, 47.64; H, 4.00; N, 4.27. Found: C, 47.54; H, 4.10; N, 3.89%. DSC: $T_{\text{onset}} = 87.6 \,^{\circ}\text{C}$, $T_{\text{max}} = 99.0 \,^{\circ}\text{C}$, $\Delta H = 63.9 \,\text{cal/g}$ (41.9 kcal/mole). IR (KBr, cm⁻¹): 1286.4 w, 980.7 w, 851.5 w, 785.9 m, 608.5 m. UV–Vis (CH₂Cl₂, λ_{max} , nm (ε , M⁻¹ cm⁻¹)): 238, 268sh (27856, 10585) ¹H NMR (CD₂Cl₂, 400 MHz) δ 1.86 (d, 4H), 7.30 (t, 8H), 7.38–7.48 (m, 12H); ¹³C NMR (CD₂Cl₂, 100 MHz) δ 133, 132, 129, 128, 15.2. ³¹P NMR (CD₂Cl₂, 161.9 MHz) δ –11.6.

4.2.3. $Pt(dppf)(N_2O_2)$ (2c)

Pt(dppf)Cl₂ (0.103 g, 0.13 mmol), and 0.087 g, 0.27 mmol of **4** are treated as for **2a** to give 0.69 g,79% **2b** as yellow crystals. *Anal.* Calc. for PtFeP₂C₃₄H₃₈N₂O₂: C, 49.83; H, 4.67, N, 3.42. Found: C, 50.15; H, 3.87; N, 3.55%. DSC: $T_{\text{onset}} = 85.1 \,^{\circ}\text{C}$, $T_{\text{max}} = 99.0 \,^{\circ}\text{C}$, $\Delta H = -52.5 \,\text{cal/g}$, 43.1 kcal/mol. IR (KBr, cm⁻¹): 1330.5 m, 974 m, 890 s, 780.1 s, 611 s. UV–Vis (CH₂Cl₂, λ_{max} , mm (ε , M⁻¹ cm⁻¹)): 238, 268sh (27856, 10585) ¹H NMR (CD₂Cl₂, 400 MHz) δ 7.71 (m, 4H), 7.50 (m 8H), 7.40 (m, 8H), 4.41 (m, 4H), 4.24(d, $J = 1.8 \,\text{Hz}$, 4 H); ¹³C NMR (CD₂Cl₂, 100 MHz) δ 145.7, 134.8, 131.8, 128.8, 77.4 (d, $J = 21 \,\text{Hz}$), 76.4 (t, J = 2H), 74.2. ³¹P NMR (CD₂Cl₂, 161.9 MHz) δ 4.7 (¹ $J_{\text{PtP}} = 3625.5 \,\text{Hz}$).

4.2.4. $Ni(dppe)(N_2O_2)$ (2d)

Ni(dppe)Cl₂ (0.2581 g, 0.489 mmol) was dissolved in acetonitrile (120 mL) and a solution of sodium-(Z)-1-{4-(2,6-di-*tert*-butyl-4-methoxycyclohexadienonyl)}diazen-1-ium-1,2-diolate (0.3127 g, 0.982 mmol) in 50 mL of methanol was added under nitrogen with constant stirring. The solution immediately turns from reddish to yellow or orange color and stirred for about 15–20 min. The solvent was removed in vacuo. The crude yellow solid material was dissolved in methylene chloride and allowed to stand for 10 min, and the solution filtered to remove any insoluble material. The solvent was removed in vacuo. The crude yellow the ther until the ether

washing is colorless. (Yield: 0.216 g, 77%), *Anal.* Calc. for NiP₂C₂₆H₂₄N₂O₂: C, 60.39; H, 4.68; N, 5.42. Found: C, 59.59; H, 4.73; N, 4.92%. DSC: $T_{\text{onset}} = 97.3 \text{ °C}$, $T_{\text{max}} = 104.1 \text{ °C}$, $\Delta H = 136.9 \text{ cal/g}$ (70.8 kcal/mole). IR (KBr, cm⁻¹): New hyponitrite bands are obscured by dppe bands. UV–Vis (CH₂Cl₂, λ_{max} , nm (ε , M⁻¹ cm⁻¹)): 236, 268, 408 (29513, 19539, 1012). ¹H NMR (CD₂Cl₂, 400 MHz) δ 2.43 (d, 4H), 7.45–7.52 (m, 12H), 7.87–7.91 (m, 8H); ¹³C NMR (CD₂Cl₂, 100 MHz) δ 133, 132, 130, 129, 25.9, ³¹P NMR (CD₂Cl₂, 161.9 MHz) δ 46.4.

4.2.5. $Ru(dppf)(NO)_2$ (3c)

Ru(NO)₂(PPh₃)₂, **3a**, 81 mg, 0.012 mmol, and 1.2 equiv. of dppf, 74 mg, 0.014 mmol, were heated at reflux for 14 h in 20 mL toluene under an atmosphere of nitrogen. After cooling the mixture was brought out of the inert atmosphere box and the solvent removed in vacuo to give a crude red-orange product which was dissolved in 10 mL dichloromethane and recrystallized by the addition of 20 mL ethanol and concentration on a rotory evaporator to give 132 mg, of 3c in 85% yield. Crystals suitable for X-ray diffraction were grown from dichloromethane/ethanol. Anal. Calc. for C34H28FeN2O2P2Ru: C, 56.29; H, 5.28; N, 3.86. Found: C, 56.52; H, 3.87; N, 3.54%. IR (cm⁻¹), KBr pellet: v(NO):1673.2s, 1629.8s, other characteristic bands: 3350 br, 1304.8w, 1264.3w,1164.9m, 836.1w, 819.7m. UV–Vis (CH₂Cl₂), λ_{max} , nm (ε , $M^{-1} cm^{-1}$): 422 (1330) ¹H NMR (CDCl₃, 400 MHz) δ 4.31 (t, J = 1.7, 4H), 4.24 (dd, J = 1.7, 1.9, 4H), 7.35– 7.37 (m, 12H), 7.53–7.58 (m, 8H); ¹³C NMR (CDCl₃, 100 MHz) δ 71.8(s), 75.1 (t, J = 4.9), 84.17 (d, J = 51.4), 128.4 (t, J = 5.8), 130.1 (s), 133.6 (t, J = 6.7), 136.4 (dd, J = 46.3, 4.5) ³¹P NMR (CDCl₃, 161.9 MHz) δ 47.5.

4.2.6. Os(dppe)(NO)₂ (3d)

 $Os(NO)_2(PPh_3)_2$, (3b) 65 mg, 0.0084. mmol, and 2.5 equiv. of bisdiphenylphosphinoethane, dppe, 83 mg, 0.0021 mmol, were heated at reflux for 30 h in 15 mL toluene under an atmosphere of nitrogen. After cooling the mixture was stripped of solvent and the residue crystallized twice in the inert atmosphere box from dichloromethane and ethanol to give 45 mg of 3d as oxygen sensitive redbrown crystals in 82% yield. Crystals suitable for X-ray diffraction were grown from dichloromethane/ethanol. Anal. Calc. for C₂₆H₂₄N₂O₂P₂Os: C, 47.99; H, 3.72; N, 4.31. Found: C, 48.28; H, 3.97; N, 4.33%. IR (cm⁻¹), KBr pellet: v(NO): 1656.8s, 1604.7s. UV–Vis (CH₂Cl₂), λ_{max} 288 nm. ¹H NMR (CD₂Cl₂, 400 MHz) δ 2.51 (d, 4H), 7.48–7.56 (m, 12H), 7.93–7.99 (m, 8H); ¹³C NMR (CD₂Cl₂, 100 MHz) δ 134, 132, 130, 127, 28.1, ³¹P NMR (CD₂Cl₂, 161.9 MHz) δ 31.4.

4.3. Reaction of hyponitrite complexes (2) with electrophiles

Reaction of HCl with $Pt(PPh_3)(N_2O_2)$ to give cis- $Pt(PPh_3)_2Cl_2$: **2a** (0.05 g, 0.07 mmol) was dissolved in CH₂Cl₂ (2 mL). HCl (0.15 mmol) in CH₃OH (0.17 mL) was added; gas was observed and a light beige precipitate formed. The solid was collected and washed with hexanes. Yield: 25 mg (40%). The identity of $cis-Pt(PPh_3)_2Cl_2$ was confirmed by the absence of the IR bands characteristic of **2a**, as well as a comparison with the literature ³¹P NMR spectrum of cis-Pt(PPh_3)_2Cl_2 as prepared by Goel [55].

Compounds 2a-c (0.05 g) were each suspended in ethanol and treated with dilute HCl solution. There was immediate effervescence with gas evolution. The solid residue was collected and characterized by NMR, IR and compared with respective authentic dichloride samples. In order to analyze the evolved gas upon addition of dilute HCl solution, about 0.02 g of compound (2a) was placed in an IR gas chamber and HCl gas was bubbled into the gas chamber. The analysis of the evolved gas by FT-IR confirms the presence of N₂O.

Reaction of iodine with $Pt(PPh_3)_2(N_2O_2)$ to give trans- $Pt(PPh_3)_2I_2$: **2a** (0.1 g, 0.13 mmol) and triethylamine (0.05 mL) were dissolved in methylene chloride (10 mL), and degassed by freeze-thaw cycles. The amine is a preventative measure to ensure that the solution remains basic. The solution was cooled to -78 °C and iodine (0.07 g, 0.26 mmol) was added. The reaction was allowed to warm to room temperature over the span of 1 h. A bright yellow precipitate formed and was collected by filtration. Yield: 0.056 g (45%) which is spectroscopically identical by IR, and ³¹P NMR to literature results for $Pt(PPh_3)_2I_2$ [56] this same product is the only isolable compound from the reaction of methyliodide or hydroiodic acid with 2a. In the case of methyl iodide there is no evidence for a transitory product corresponding[31] to *trans*-Pt(PPh₃)₂(CH₃)I as its peak at 28.1 ppm (${}^{1}J_{Pt-P} = 3460 \text{ Hz}$) was not seen by ${}^{31}P$ NMR of the monitored reaction mixtures which are dominated by peaks corresponding to the starting material and diiodide product.

4.4. The stoichiometry of the reaction between $Pt(PPh_3)_2(N_2O_2)$ with iodine

The platinum complex **2a** (0.025 g, 0.032 mmol) was dissolved in CD_2Cl_2 (0.5 mL) in an NMR tube. Iodine (0.004 g, 0.016 mmol) was added and the mixture was sonicated for 3 h. Once all of the *cis*-hyponitrite had reacted, as confirmed by ³¹P NMR, a solution of triphenylphosphine sulfide (0.018 g, 0.061 mmol) in CD_2Cl_2 (0.3 mL) was added to the NMR tube and the ³¹P NMR was measured, with a delay time of 1 s. The integration between triphenylphosphine sulfide and triphenylphosphine oxide was measured and compared to the expected value. Expected ratio (P(S)Ph_3:P(O)Ph_3) 1.9:1. Measured ratio (P(S)Ph_3: P(O)Ph_3) 2.1:1.

Reaction of $Pt(PPh_3)_2(N_2O_2)$ with $CF_3SO_3CH_3$: **2a** (0.1 g, 0.13 mmol) was dissolved in methylene chloride (5 mL), and degassed through freeze-thaw methods. The solution was cooled to $-78 \,^{\circ}\text{C}$ and $CF_3SO_3CH_3$ (0.02 mL, 0.2 mmol) was added. The reaction was allowed

to warm to room temperature in the absence of light over 12 h. The white precipitate which formed was collected filtration. Yield: 0.065 g (71%). The precipitate is insoluble in organic solvents, alcohols, water, acetonitrile, and DMSO. On the basis of IR the compound is determined to be $[Pt(PPh_3)_2(\mu-OH)]_2[OSO_2CF_3]_2$. IR (KBr, cm⁻¹): 3548 m (v_{OH}) , 1273vs (v_{SO}) , 1032vs (v_{SO}) . An authentic sample of the product was also synthesized for comparison by treating, Pt(PPh₃)Cl₂ (0.05 g, 0.06 mmol), in 20 mL chloroform/ acetone (1:1) to which water (1 mL) and AgOSO₂CF₃ (0.02 g, 0.06 mmol) were then added. After 1 h the silver chloride precipitate was removed by filtration through diatomaceous earth and diethyl ether (10 mL) was added to the filtrate. On standing for 12 h, a white precipitate of $[Pt(PPh_3)_2(\mu-OH)]_2[OSO_2CF_3]_2$ was collected whose IR spectrum contained the same v_{OH} band at 3550 cm⁻¹. This band is also present in [Pt(PPh₃)₂(µ-OH)]₂[BF₄]₂, prepared by Phillips and coworkers [57].

5. X-ray crystallographic data

X-ray diffraction data for $2 \cdot CH_2Cl_2$, 3c, and 3d were collected on a Bruker P4 diffractometer equipped with a molybdenum tube and a graphite monochromator, Table 1 contains diffraction data for $2 \cdot CH_2Cl_2$, 3c, and 3d. Unit-cell dimensions were determined from several accurately centered reflections in high 2θ angles using XSCANS

program. Three standard reflections measured after every 97 reflections exhibited no significant loss of intensity. The data were corrected for Lorentz-polarization effects and absorption. The structure was solved by direct methods and refined by least-squares techniques on F^2 using SHELXTL.

The *cis* hyponitrite complex 2 is a redetermination of a structure originally reported [12] as a benzene solvate from crystals obtained from benzene/dichloromethane which refined to R = 10.8%. In this original structure the unit cell corresponds to the triclinic space group $P\overline{1}$, with $a = 12.199(6), b = 10.747(6), c = 15.730(8) \text{ Å}, \alpha = 108.75$ (4), $\beta = 95.57(4)$, and $\gamma = 69.98(4)^{\circ}$ with Z = 2, and V =1834.6 Å³. In our redetermination crystals were obtained from dichloromethane/ethanol and crystallize in monoclinic space group $P2_1n$, with a = 13.037(2), b = 15.685(3), c = 17.023(3) Å, $\alpha = \gamma = 90$, and $\beta = 98.020(10)^{\circ}$ with Z = 4, and $V = 3446.9(10) \text{ Å}^3$. The monoclinic form has a dichloromethane solvate that is well defined and refined anisotropically in the last least squares cycles to give a final R_1 of 3.44%, and S_{gof} of 1.027, and a relatively flat electron density map with the largest difference peak being close to the metal center.

The dinitrosyl complexes 3c and 3d were crystallized from dichloromethane/ethanol as large deep orange blocks. The diffraction data collection, solution, and refinement all followed the outline above for 2a with key data

Table 1

Crystallographic and	structure refinement	data for	compounds	2, 3c	and 3d
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	1 /				
Compound	2	3c	3d		
Molecular formula	$C_{37}H_{32}Cl_2N_2O_2P_2Pt$	$C_{34}H_{30}FeN_2O_3P_2Ru$ $C_{26}H_{24}N_2O_2O_3P_2$			
Formula weight	864.58	733.46	648.61		
Temperature (K)	293(2)	293(2)	293(2)		
Crystal system	monoclinic	triclinic	monoclinic		
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$		
$a(\mathbf{A})$	13.037(2)	9.363(3)	13.617(3)		
b (Å)	15.685(3)	11.892(2)	11.964(2)		
$c(\mathbf{A})$	17.023(3)	14.870(3)	15.932(3)		
α (°)	90	78.29(1)	90		
β (°)	98.020(10)	86.38(2)	105.22(2)		
γ (°)	90	88.50(2)	90		
$V(Å^3)$	3446.9(10)	1617.9(6)	2504.5(8)		
Z	4	2	4		
$\rho_{\rm calc} ({\rm Mg/m^3})$	1.666	1.506	1.720		
$\mu (\mathrm{mm}^{-1})$	4.355	1.050	5.245		
F(000)	1704	744	1264		
Crystal size (mm)	$0.26 \times 0.20 \times 0.14$	$0.70 \times 0.24 \times 0.20$	$0.28 \times 0.22 \times 0.20$		
2θ Range (°)	3.54-49.88	4.02-50.00	3.50-50.02		
Index ranges	$-1 \leqslant h \leqslant 14, -1 \leqslant k \leqslant 16,$	$-1 \leqslant h \leqslant 11, -13 \leqslant k \leqslant 13,$	$-16 \leqslant h \leqslant 1, -1 \leqslant k \leqslant 14,$		
-	$-18 \leqslant l \leqslant 20$	$-17 \leq l \leq 17$	$-18 \leqslant l \leqslant 18$		
Reflections collected	5853	7074	5458		
Independent reflections $[R_{int}]$	4477 [0.0310]	5663 [0.0229]	4362 [0.0250]		
Absorption correction type	psi-scan	psi-scan	psi-scan		
Maximum and minimum transmissions	0.1617 and 0.1108	0.3908 and 0.3376	0.1478 and 0.1180		
Refinement method	least-squares on F^2	least-squares on F^2	least-squares on F^2		
Data/restraints/parameter	4477/0/415	5663/0/388	4362/0/298		
Goodness-of-fit on F^2	1.027	1.093	1.006		
$R\left[I > 2\sigma I\right]$	$R_1 = 0.0344, wR_2 = 0.0815$	$R_1 = 0.0494, wR_2 = 0.1397$	$R_1 = 0.0296, wR_2 = 0.0607$		
R (all data)	$R_1 = 0.0422, wR_2 = 0.0867$	$R_1 = 0.0607, wR_2 = 0.1490$	$R_1 = 0.0494, wR_2 = 0.0670$		
Largest difference in peak and hole ($e \text{ Å}^3$)	2.857 and - 0.955	1.995 and -0.512	0.607 and -0.772		

collected in Table 1. During the final stages of the refinement of 3c an extra intense solvate peak was located in electron difference maps and was modeled as a water solvate whose presence was confirmed by measurement of the IR spectrum of other crystals from the same batch which have a band at 3350 cm⁻¹ attributable to the water solvate.

6. Supplementary material

CCDC 633311, 633312 and 635099 contain the supplementary crystallographic data for $2 \cdot 2CH_2Cl_2$, 3c and 3d. These data can be obtained free of charge via http:// www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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