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Platinum(II) Hydrazido Complexes

Aibing Xia and Paul R. Sharp*

Department of Chemistry, University of Missouri, 125 Chemistry, Columbia, Missouri 65211

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Reaction of 1,2-dimethylhydrazine with the platinum hydroxo complex [(dppp)Pt(μ-OH)]$_2$(BF$_4$)$_2$ gives the bridging 1,2-dimethylhydrazido(−2) product [(dppp)$_2$Pt$_2$(μ-η^2:η^2-MeNNMe)](BF$_4$)$_2$ **1**. Crystals of **1**·CH$_2$Cl$_2$ from CH$_2$Cl$_2$/Et$_2$O are monoclinic (*C*/2) with $a = 19.690(1)$, $b = 18.886(1)$, $c = 17.170$ (1) Å, and $\beta = 92.111(1)°$. Treatment of [(dppp)Pt(μ-OH)]$_2$(OTf)$_2$ with 1,1-dimethylhydrazine gives [(dppp)$_2$Pt$_2$(μ−OH)(μ−NHNMe$_2$)](OTf)$_2$ **2**. Crystals of **2**·CH$_2$Cl$_2$ from CH$_2$Cl$_2$/Et$_2$O are triclinic (*P*-1) with $a = 12.910$ (3), $b = 13.927(3)$, $c = 17.5872$ (3) Å, $\alpha = 87.121(3)$, $\beta = 89.997(4)$, and $\gamma = 84.728(3)°$. Reaction of [(dppp)Pt(μ-OH)]$_2$(OTf)$_2$ with 1 equiv of phenylhydrazine in CH$_2$Cl$_2$ gives [(dppp)$_2$Pt$_2$(μ-OH)(μ-NHNHPh)](OTf)$_2$ **3**. Two equivalents of phenylhydrazine with [(dppp)Pt(μ-OH)]$_2$(X)$_2$ gives [(dppp)Pt(μ-NHNHPh)]$_2$(X)$_2$ **4** (X = BF$_4$, OTf). Crystals of **3**·ClCH$_2$CH$_2$Cl from ClCH$_2$CH$_2$Cl/^{i}Pr$_2$O are monoclinic ($P2_1/n$) with $a = 20.990(2)$, $b = 13.098(1)$, $c = 25.773$ (2) Å, and $\beta = 112.944(2)°$. Crystals of **4**(X = BF$_4$)·ClCH$_2$CH$_2$Cl·2(^{t}BuOMe) from ClCH$_2$CH$_2$Cl/^{t}BuOMe are monoclinic (*C*2/*m*) with $a = 30.508(1)$, $b = 15.203(1)$, $c = 19.049$ (1) Å, and $\beta = 118.505(2)°$.

Introduction

Transition metal complexes containing metal bonded N$_2$ units are important in dinitrogen activation and reduction. As a result, N$_2$ coordination chemistry is of great interest to chemists.[1−9] Hydrazido metal complexes are critical models for intermediates in dinitrogen reduction. The crystal structure determination of the nitrogenase FeMo cofactor has revealed an Fe$_7$MoS$_9$ cluster[10,11] at the active center where dinitrogen coordinates and is reduced. With the likely involvement of multimetal center dinitrogen bonding to this cluster, both initially and during dinitrogen reduction,[12−15] polymetallic hydrazido complexes have taken on a new importance in dinitrogen reduction modeling. While there are a number of known polymetallic hydrazido complexes that may serve as models for nitrogenase dinitrogen reduction, the bulk of these involve early transition metal systems. Very few complexes past group seven are known, yet late transition metal complexes may reveal new bonding modes to consider in dinitrogen reduction.[16]

In previous work we showed that the oxo complex [(LAu)$_3$(μ-O)]$^+$ (L = a phosphine) is an excellent reagent for the formation of complexes with multisite Au−N bonding and that the reaction of the oxo complex with hydrazines yields a series of these complexes. The type of complex isolated depends on the hydrazine substitution. With unsubstituted hydrazine, the first group 11 dinitrogen complexes [(LAu)$_6$(μ-N$_2$)]$^{2+}$ were obtained,[16−18] while with substituted hydrazines either the trimetallic hydrazido complexes,[17−19] [(LAu)$_3$(μ-NNR$_2$)]$^+$ or rearranged semidine complexes[20] [(LAu)$_3$(μ-NC$_6$H$_4$NHPh)]$^+$, were isolated. Similar exchange reactions with the platinum hydroxo complexes [L$_2$Pt(μ-OH)]$_2$$^{2+}$ (L$_2$ = a bidentate diphosphine) and hydrazine yielded the dimetallic dihydrazido complexes [L$_2$Pt(μ-NHNH$_2$)]$_2$$^{2+}$.[21] Given the scarcity of late transition metal polymetallic hydrazido complexes, and the differences in the gold oxo hydrazine reaction chemistry with hydrazine substitution, we have extended our investigation of the platinum system to reactions of [L$_2$Pt(μ-OH)]$_2$$^{2+}$ (L$_2$ = dppp) with substituted hydrazines. The formation and characterization of a bridging side-on 1,2-dimethylhydrazido complex and bridging end-on 1,1-dimethylhydrazido and phenylhydrazido complexes are described herein.

Results

Reaction of the platinum hydroxo complex[22,23] [(dppp)Pt(μ-OH)]$_2$(BF$_4$)$_2$ with the symmetric hydrazine 1,2-dimethylhydra-

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*To whom correspondence should be addressed. E-mail: SharpP@missouri.edu.

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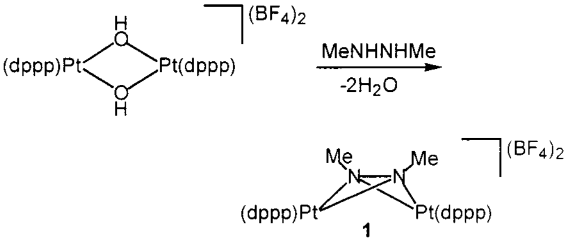
Table 1. Crystallographic and Data Collection Parameters

formula	$C_{59}H_{60}B_2F_8N_2P_4Pt_2 \cdot CH_2Cl_2$ (**1**)	$C_{58}H_{60}F_6N_2O_7P_4Pt_2S_2 \cdot CH_2Cl_2$ (**2**)	$C_{63}H_{60}Cl_{2.5}F_6N_2O_7$-$P_4Pt_2S_2C_2H_4Cl_2$ (**3**)	$C_{77}H_{91}B_2Cl_2$-$F_8N_4O_3P_4Pt_2$ (**4**)
fw	1545.7	1674.2	1737.9	1879.1
space group	*C*2/*c*	*P*-1	$P2_{1/n}$	*C*2/*m*
T, °C	−100	−100	−100	−100
a, Å	18.690(1)	12.910(3)	20.990(2)	30.508(1)
b, Å	18.886(1)	13.927(3)	13.098(1)	15.203(5)
c, Å	17.170(1)	17.587(3)	25.773(2)	19.049(1)
α, deg	90	87.121(3)	90	90
β, deg	92.111(1)	89.997(4)	112.944(2)	118.505(1)
γ, deg	90	84.728(3)	90	90
V, Å^3	6056(1)	3144(1)	6525(1)	7764(1)
Z	4	2	4	4
d_{calc}, g/cm3	1.695	1.768	1.769	1.608
μ, mm-1	4.87	4.77	4.62	3.82
λ (Mo Kα), Å	0.71073	0.71073	0.71073	0.71073
R1^a	0.0397	0.0530	0.0504	0.0478
wR2^b(obs)	0.1259	0.1450	0.1310	0.1390

[a] $R1 = (\sum||F_o| - |F_c||)/\sum|F_o|$. [b] $wR2 = [(\sum w(F_o^2 - F_c^2)^2)/\sum w(F_c^2)^2]^{1/2}$, with weight $= 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$; $x = 0.0526$, $y = 7.5107$ for **1**; $x = 0.1000$, $y = 0$ for **2**; $x = 0.0735$, $y = 0$ for **3**; $x = 0.0584$, $y = 0$ for **4**; $P = (F_o^2 + 2F_c^2)/3$.

zine in CH_2Cl_2 gives a white product, **1**. Product **1** is soluble in DMSO but only slightly soluble in CH_2Cl_2 and THF. NMR data indicate the presence of a Pt bound chelated dppp ligand[24] and incorporation of dimethylhydrazine. Integration of the dppp and the hydrazine methyl group signals indicate a 2−to−1 value for the dppm−to−dimethylhydrazine ratio. This information and elemental analysis suggest the identity of **1** as the 1,2-dimethylhydrazido(−2) complex $[(dppp)_2Pt_2(\mu\text{-}\eta^2{:}\eta^2\text{-}MeNNMe)](BF_4)_2$ (eq 1).



(1)

This formulation and the presence of the side-bonded bridging 1,2-dimethylhydrazido ligand is confirmed by an X-ray single-crystal structure determination (Figure 1). An abbreviated summary of crystal data collection and processing is given in Table 1. Selected bond distances and angles are listed in Table 2. The structure shows a square-planar edge-shared Pt dimer. Such structures can be planar or folded along the shared edge depending on factors such as the metal, the ligands, and steric interactions.[25−27] Complex **1** shows a nonplanar structure with a fold angle of 112.5°. Other aspects of the structure are discussed below.

In an attempt to reductively cleave its N−N bond, **1** was treated with Li in THF. This afforded gray Pt metal and the Pt(0) complex $(dppp)_2Pt$, whose identity was confirmed by an X-ray single-crystal structure analysis.[28] The fate of the dimethylhydrazido ligand was not determined.

Treatment of a CH_2Cl_2 solution of $[(dppp)Pt(\mu\text{-}OH)]_2(OTf)_2$ with 1 equiv of the unsymmetrical hydrazine 1,1-dimethylhydrazine gives the hydrazido(−1) hydroxo complex $[(dppp)_2Pt_2(\mu\text{-}OH)(\mu\text{-}NHNMe_2)](OTf)_2$, **2** (eq 2).

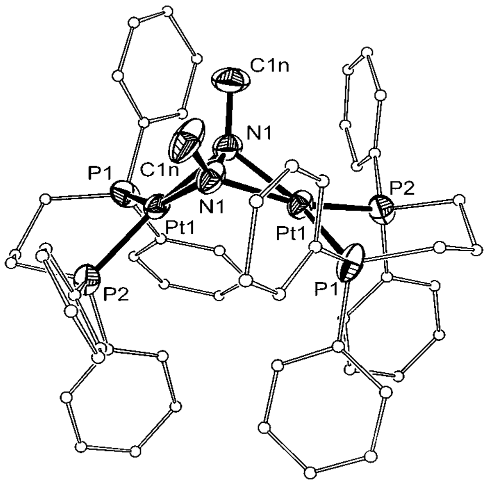
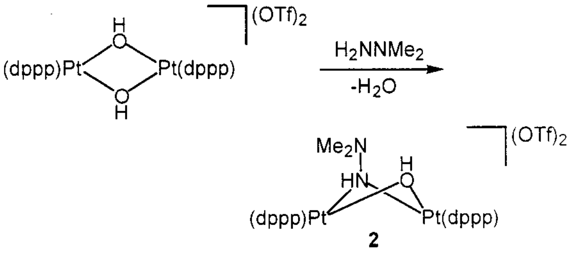


Figure 1. ORTEP drawing of the cationic portion of $[(dppp)_2Pt_2(\mu\text{-}\eta^2{:}\eta^2\text{-}MeNNMe)](BF_4)_2$ **1**. Here and in the following figures, non-carbon and non-hydrogen atoms are represented by 50% probability thermal ellipsoids.

Table 2. Selected Distances (Å) and Angles (Deg) for $[(dppp)_2Pt_2(\mu\text{-}\eta^2{:}\eta^2\text{-}MeNNMe)](BF_4)_2$ **1**

Pt1−Pt1′	3.220(1)	Pt1−N1	2.039(5)
Pt1′−N1	2.089(5)	Pt1−P1	2.233(2)
Pt1−P2	2.239(2)	N1−C1*n*	1.473(8)
N1−N1′	1.429(11)		
P1−Pt1−P2	92.69(6)	N1−Pt1−N1′	40.4(3)
Pt1−N1−C1*n*	131.6(4)	Pt1′−N1−C1*n*	125.8(4)
N1−Pt1−P1	111.1(2)	N1′−Pt1−P2	115.9(2)
C1*n*−N1−N1′	120.8(4)	Pt1−N1−Pt1′	102.5(2)



(2)

The presence of two different bridging groups is readily detected in the ^{31}P NMR spectra of **2**, which shows two

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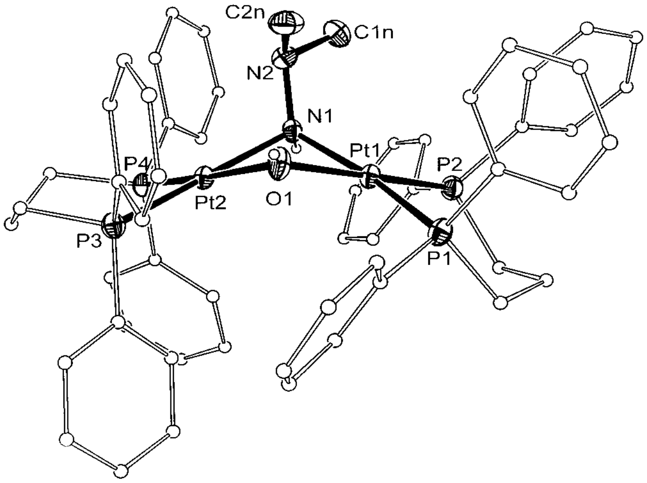


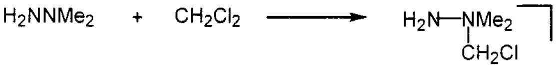
Figure 2. ORTEP drawing of the cationic portion of [(dppp)$_2$Pt$_2$(μ-OH)(μ-NHNMe$_2$)](OTf)$_2$ **2**.

Table 3. Selected Distances (Å) and Angles (Deg) for [(dppp)$_2$Pt$_2$(μ-OH)(μ-NHNMe$_2$)](OTf)$_2$ **2**

Pt1−Pt2	3.0867(5)	Pt1−N1	2.111(5)
Pt2−N1	2.105(5)	Pt1−O	2.095(4)
Pt2−O	2.104(4)	Pt1−P1	2.258(2)
Pt1−P2	2.230(2)	Pt2−P3	2.259(2)
Pt2−P4	2.208(2)	N1−N2	1.469(7)
N2−C1*n*	1.433(9)	N2−C2*n*	1.458(9)
P1−Pt1−P2	92.99(6)	P3−Pt2−P4	93.46(6)
P1−Pt1−O	92.35(1)	P3−Pt2−O	94.17(13)
P2−Pt1−O	174.2(1)	P4−Pt2−O	172.4(1)
P1−Pt1−N1	168.3(1)	P3−Pt2−N1	170.1(1)
P2−Pt1−N1	98.35(13)	P4−Pt2−N1	96.21(14)
O−Pt1−N1	76.22(17)	O−Pt2−N1	76.15(18)
Pt1−O−Pt2	94.65(17)	Pt1−N1−Pt2	94.12(20)
Pt1−N1−N2	121.9(4)	Pt2−N1−N2	112.3(3)
N1−N2−C1*n*	109.6(5)	N1−N2−C2*n*	110.4(5)

phosphorus signals as doublets, each with ^{195}Pt satellites. The signal with the smaller P−Pt coupling is assigned to the phosphorus atoms trans to the more strongly donating hydrazido ligand.[29−31] The structure of **2** was determined by X-ray single-crystal diffraction methods and is shown in Figure 2. An abbreviated summary of crystal data collection and processing is given in Table 1. Selected bond distances and angles are listed in Table 3. Again, the structure is typical of square-planar edge-shared Pt dimers. Unlike in **1**, the hydrazido ligand in **2** is not side-bonded and bridges through a single nitrogen atom. Details of the structure are discussed below.

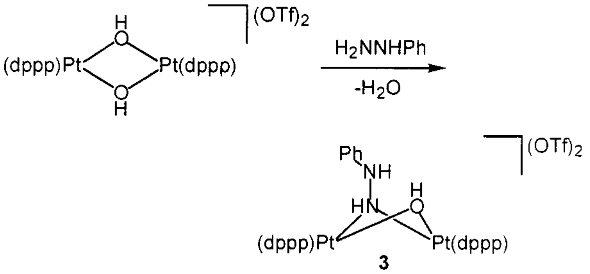
Further reaction of 1,1-dimethylhydrazine in CH$_2$Cl$_2$ with **2** at ambient temperatures did not give the expected second hydroxo−hydrazido exchange and the bis(1,1-dimethylhydrazido(−1)) complex [(dppp)Pt(μ-NHNMe$_2$)]$_2$(OTf)$_2$. Instead, (dppp)PtCl$_2$ was obtained. The source of the chloride ion in the formation of (dppp)PtCl$_2$ in the reaction of **2** with excess 1,1-dimethylhydrazine in CH$_2$Cl$_2$ (eq 2) is apparently the CH$_2$Cl$_2$ solvent. A solution of 1,1-dimethylhydrazine in CH$_2$Cl$_2$ rapidly produces the adduct [Me$_2$N(CH$_2$Cl)NH$_2$]Cl (eq 3), as determined by NMR analysis and a single-crystal X-ray diffraction experiment (Supporting Information). Complex **2** did not react further with excess NH$_2$NMe$_2$ in either THF or *o*-dichlorobenzene. Heating **2** in *o*-dichlorobenzene at 80 °C overnight leads to loss of all ^{31}P NMR signals and formation of a black precipitate.



$$H_2NNMe_2 + CH_2Cl_2 \longrightarrow \left[H_2N{-}\underset{CH_2Cl}{\underset{|}{N}}Me_2\right]Cl \qquad (3)$$

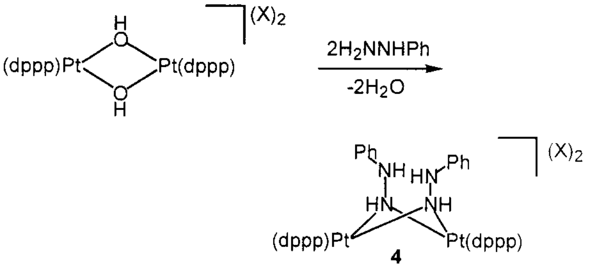
Curious about the facile reaction between 1,1-dimethylhydrazine and CH$_2$Cl$_2$, we investigated two other chlorinated hydrocarbons. With ClCH$_2$CH$_2$Cl, [Me$_2$N(CH$_2$CH$_2$Cl)NH$_2$]Cl was obtained. However, NH$_2$NMe$_2$ did not react with *o*-dichlorobenzene, even after heating for one week at 160 °C. Reactions of 1,1-dimethylhydrazine with chlorinated hydrocarbons have previously been described in a patent application.[32]

Reactions of [(dppp)Pt(μ-OH)]$_2$$^{2+}$ with phenylhydrazine follow more expected lines. With 1 equiv of phenylhydrazine, hydroxo hydrazido(−1) complex [(dppp)$_2$Pt$_2$(μ-OH)(μ-NHNHPh)](OTf)$_2$, **3**, is obtained (eq 4) from [(dppp)Pt(μ-OH)]$_2$(OTf)$_2$.



(4)

Two equivalents or excess phenylhydrazine with [(dppp)Pt(μ-OH)]$_2$(X)$_2$ gives the dihydrazido(−1) complex, [(dppp)Pt(μ-NHNHPh)]$_2$(X)$_2$, **4** (X = BF$_4$, OTf; eq 5).



(5)

The hydroxo hydrazido(−1) complex **3** can also be obtained by the conproportionation of [(dppp)Pt(μ-OH)]$_2$$^{2+}$ and **4** in CH$_2$Cl$_2$ (2 d). The structures of **3** (Figure 3) and **4** (X = BF$_4$, Figure 4) were determined by single-crystal X-ray diffraction experiments. An abbreviated summary of crystal data collection and processing is given in Table 1. Selected bond distances and angles are listed in Tables 4 and 5.

Discussion

The formation of the hydrazido complexes in the above reactions may be viewed as a deprotonation of the hydrazine by the basic hydroxo ligands. This approach, the reaction of a basic ligand complex with hydrazines, has been used in several other systems for the preparation of transition metal hydrazido complexes. We have previously used Pt[21] and Au[17−19] complexes with basic hydroxo or oxo ligands in the formation of hydrazido complexes. Others have used basic alkyl,[33] oxo,[34−40]

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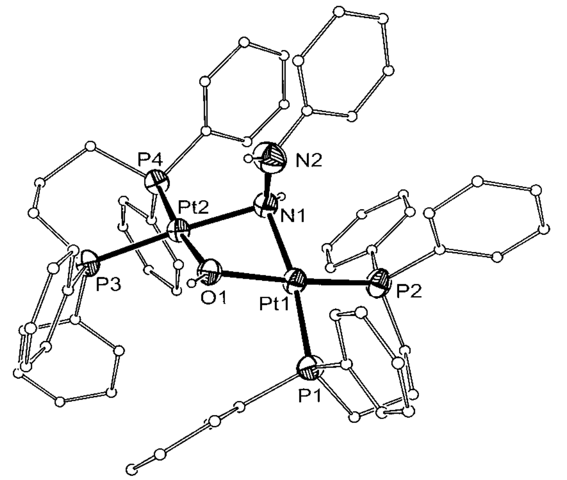


Figure 3. ORTEP drawing of the cationic portion of $[(dppp)_2Pt_2(\mu\text{-}OH)(\mu\text{-}NHNHPh)](OTf)_2$ **3**.

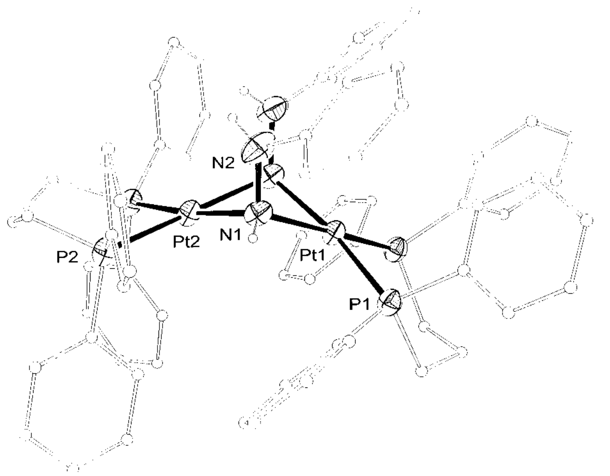


Figure 4. ORTEP drawing of the cationic portion of $[(dppp)Pt(\mu\text{-}NHNHPh)]_2(BF_4)_2$ **4**.

and amido[41] ligand complexes to produce mostly terminal hydrazido complexes.

One of the notable features of the reactions in the current study is the product variation with the substituents on the hydrazine. In our earlier work with unsubstituted hydrazine, the sole observed products were the dihydrazido complexes $[L_2Pt(\mu\text{-}NHNH_2)]_2^{2+}$, analogous to **4**.[21] With the substituted hydrazines studied here, the mixed hydrazido hydroxo complexes **2** and **3** are observed. This may be explained in steric terms, where the second substitution of the hydroxo group by the hydrazido group is slowed ($PhHNNH_2$) or stopped completely (Me_2NNH_2). We have previously observed steric inhibition in reactions of the hydroxo complexes with anilines, where mixed hydroxo–amido complexes were isolated.[21] Driver and Hartwig have studied hydroxo–amido exchange reactions in related Pd complexes and have found that these reactions are initiated by bridge cleavage.[42] Scheme 1 illustrates a likely pathway, derived from Driver and Hartwig's work, for the hydroxo–hydrazido exchange reactions in the current Pt system. Possible steric inhibition in the second hydrazine coordination step is apparent.

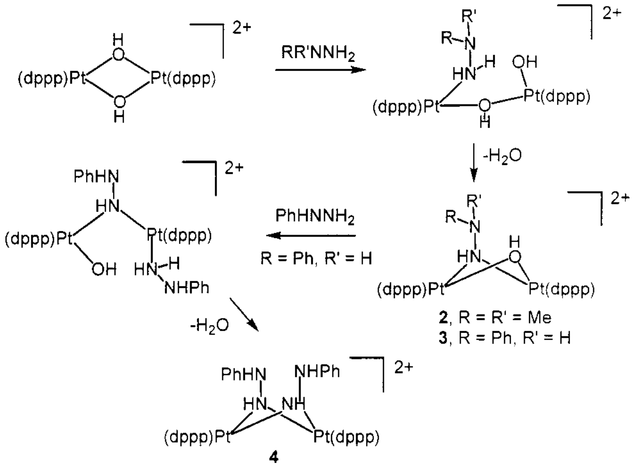
Table 4. Selected Distances (Å) and Angles (Deg) for $[(dppp)_2Pt_2(\mu\text{-}OH)(\mu\text{-}NHNHPh)](OTf)_2$ **3**

Pt1–Pt2	3.0647(5)	Pt1–N1	2.105(6)
Pt2–N1	2.108(6)	Pt1–O	2.093(5)
Pt2–O	2.111(5)	Pt1–P1	2.250(2)
Pt1–P2	2.217(2)	Pt2–P3	2.240(2)
Pt2–P4	2.222(2)	N1–N2	1.496(10)
P1–Pt1–P2	92.70(8)	P3–Pt2–P4	91.00(7)
P1–Pt1–O	93.20(2)	P3–Pt2–O	95.74(2)
P2–Pt1–O	174.0(2)	P4–Pt2–O	172.6(1)
P1–Pt1–N1	169.3(2)	P3–Pt2–N1	171.3(2)
P2–Pt1–N1	97.97(17)	P4–Pt2–N1	97.50(17)
O–Pt1–N1	76.12(21)	O–Pt2–N1	75.68(21)
Pt1–O–Pt2	93.60(21)	Pt1–N1–Pt2	93.36(24)
Pt1–N1–N2	112.3(5)	Pt2–N1–N2	107.3(4)
N1–N2–C1	119.6(7)		

Table 5. Selected Distances (Å) and Angles (Deg) for $[(dppp)Pt(\mu\text{-}NHNPh)]_2(BF_4)_2$ **4**

Pt1–Pt2	3.0687(5)	Pt1–N1	2.110(5)
Pt2–N1	2.105(5)	Pt1–P1	2.273(2)
Pt2–P2	2.259(2)	N1–N2	1.455(7)
P1–Pt1–P1′	93.13(8)	P2–Pt2–P2′	92.85(9)
P1–Pt1–N1	95.58(15)	P2–Pt2–N1	95.75(16)
P1–Pt1–N1′	169.8(2)	P2–Pt2–N1′	170.8(2)
N1′-Pt1–N1	75.3(3)	N1′-Pt2–N1	75.5(3)
Pt1–N1–Pt2	93.4(2)	Pt1–N1–N2	116.9(4)
Pt2–N1–N2	108.0(4)	N1–N2–C1	117.1(5)

Scheme 1



More difficult to explain is the formation of the side-bonded hydrazido complex **1**. Two possible pathways for the formation of **1** are shown in Scheme 2. In path A, the formation of **1** is preceded by the formation of a hydroxo hydrazido(−1) complex **5** analogous to **3**. Sterics would disfavor formation of a dihydrazido complex. Intermediate hydroxo hydrazido(−1) complex **5** then needs to eliminate water to form **1**. Although hydroxo hydrazido complex **2** should not be capable of following this pathway since there is no hydrogen atom available for elimination, the phenylhydrazido(−1) hydroxo **3** should be able to follow this same pathway. Yet, **3** is stable, and all attempts to force **3** to eliminate water and form a side bonded

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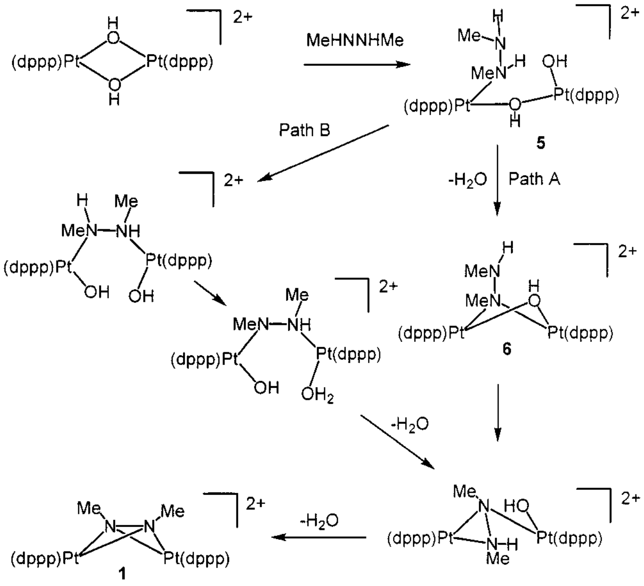
Scheme 2



hydrazido(−2) complex analogous to **1** have failed. Assuming path A in Scheme 2 is correct, an explanation is needed for why **3** fails to eliminate while intermediate **5** does. Since it has been shown that substitution in closely related Pd complexes requires bridge cleavage,[42] a difference between **3** and proposed intermediate **5** is discernible. The bridge cleavage requires attack of the free end of the hydrazido ligand on one of the Pt centers. With its electron withdrawing Ph substituent, the free end of the hydrazido ligand in **3** is less basic than the Me substituted free end in intermediate **5**. This lower basicity could suppress the bridge cleavage and formation of the side-bonded hydrazido(−2) complex. Sterics could also be a factor in this sequence, where the smaller methyl group could allow approach of the free end of the hydrazido ligand to the Pt center. Indeed, attack of the free hydrazido end must have fairly severe requirements, as it would be far from the geometry observed in the structures of **2** and **3**. Similar arguments can be made for path B to explain why phenylhydrazine fails to give an analogue of **1**.

The hydrazido(−1) bonding mode displayed by **2**−**4**, where only the deprotonated end of the hydrazido(−1) ligand bridges between two metals, is rare. The only other complex to display this bonding mode is again a late transition metal system, $[(Ph_3PAu)_2(\mu\text{-NHNPh}_2)]^+$.[17] Closely related $[(dppm\text{-H})Pt(\mu\text{-NHNH}_2)]_2$-$LiBF_4$ also shows this bonding mode, but with a Li−N interaction with the free end of the hydrazido ligands.[21] Multimetal interactions involving both ends of hydrazido(−1) ligands have been observed in Ru_3 carbonyl cluster complexes.[43−48]

The N−N bond distances in **2**−**4** are similar and range from 1.455(7) to 1.496(10) Å consistent with the single N−N bond in free hydrazines (1.45−1.46 Å).[49,50] Distances associated with the Pt centers (Pt−Pt: 3.065−3.087, Pt−O: 2.104−2.111, Pt−N: 2.105−2.108, Pt−P: 2.207−2.273 Å) in **2**−**4** are all essentially identical to those of related hydroxo−amido $[(L_2Pt)_2(\mu\text{-OH})(\mu\text{-NHR})]_2^{2+}$ and diamido $[L_2Pt(\mu\text{-NHR})]_2^{2+}$ complexes,[21] indicating little perturbation of the coordination environment of the Pt centers on replacement of the amido ligands with the hydrazido ligands.

The side-bonded bridging coordination mode of the MeNNMe unit in **1** suggests the presence of either a hydrazido(2−) or a diazo ligand. The N−N bond distance of 1.429(11) indicates that the hydrazido(2−) formulation is the best description. Shorter N−N bond distances (1.361−1.413 Å) are found in Fe_2 carbonyl complexes with this coordination mode.[51−57] These complexes are usually prepared from diazo compounds and apparently retain some diazo character. A Zr,[58] W,[33] and Sm[59,60] complex with this hydrazido(2−) bonding mode have also been reported.

Comparing the structure of **1** with **2**−**4**, **1** has a longer Pt−Pt distance (3.220 Å) and a shorter Pt−N bond (2.039 Å). Although an Fe−Fe bond is present in the Fe analogues of **1** (e.g., $[(CO)_6Fe_2(\mu\text{-}\eta^2{:}\eta^2\text{-MeNNMe})]$), a similar trend of shortened Fe−N bond distances and elongated Fe−Fe distances over simple nitrogen bridged systems was noted.[56] The greater metal−metal distance of the Pt structure is reflected in the Pt−N−Pt angle in **1** (102.5°), which is substantially larger that the Fe−N−Fe angle (83.6°) in the Fe complex.

We had anticipated that reduction of **1** with Li would result in cleavage of the N−N bond. Reductive cleavage of the Fe analogues of **1** to diimido or diamido complexes by addition of an $Fe(CO)_3$ fragment[61] or dihydrogen[62] have been reported, as have several other examples of diazo cleavage.[45,47,53,63−67] The lack of success with **1** may be due to the instability of the expected diimido product, $[(dppp)Pt(\mu\text{-NMe})]_2$. We have prepared related diimido complexes by deprotonation of diamido complexes, but not with dppp, and only for aryl imido ligands.[21,68] Future work will be directed to closing this gap between analogues of **1** and diimido complexes by using more suitable ligand systems.

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Experimental Section

General Procedures. Experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres Corp. drybox. Solvents were dried by standard techniques and stored under nitrogen over 4 Å molecular sieves. The 1,1-dimethyl hydrazine and phenylhydrazine were purchased from Aldrich Chemicals. 1,2-Dimethyl hydrazine was prepared from its HCl adduct by a modified literature procedure.[37] The hydroxo complexes $[(\mathrm{dppp})\mathrm{Pt}(\mu\text{-OH})]_2(\mathrm{X})_2$ (X = BF_4 or OTf) were prepared by literature procedures.[22] NMR spectra were recorded on a Bruker AMX-250 spectrometer. The ^{1}H NMR (250 MHz) and ^{13}C NMR (62.9 MHz) spectra are referenced to TMS or to solvent impurities referenced back to TMS; ^{31}P NMR (101 MHz) spectra are referenced to external 85% H_3PO_4. All NMR shifts are in ppm with negative shifts upfield from the reference. Infrared spectra (frequencies given in cm^{-1}) were recorded on a Nicolet 550 Magna FTIR spectrometer using KBr pellets. Spectra were recorded at ambient temperatures (22 °C) unless otherwise indicated.

Preparation of $[(\mathrm{dppp})_2\mathrm{Pt}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-MeNNMe})](\mathrm{BF}_4)_2$ 1. 1,2-Dimethylhydrazine (0.375 mL of a 0.20 M CH_2Cl_2 solution, 0.080 mmol) was added to a solution of $[(\mathrm{dppp})\mathrm{Pt}(\mu\text{-OH})]_2(\mathrm{BF}_4)_2$ (0.070 g, 0.050 mmol) in 1 mL of CH_2Cl_2. The yellow solution was stirred at ambient temperature for 2 h. Addition of Et_2O (10 mL) to the cloudy mixture afforded a white precipitate. The precipitate was collected through filtration and washed twice with Et_2O (3 mL) to obtain a light yellow solid (0.060 g, 78%). Anal. Calcd (found) for $C_{56}H_{58}B_2F_8N_2P_4Pt_2{\cdot}CH_2Cl_2$: C, 44.70 (44.52); H, 3.95 (4.04); N, 1.83 (1.83). Mp: 249−251 °C. ^{1}H NMR (DMSO-d_6): δ 1.93 (broad, 8H, PCH_2CH$_2$CH_2P), 2.77 (broad s, 6H, Me), 3.00 (broad, 4H, PCH$_2$CH_2CH$_2$P), 7.20−7.65 (m, 40H, phenyl). ^{13}C NMR (DMSO-d_6): δ 18.92 (PCH$_2$CH$_2$CH$_2$P), 22.92 (PCH$_2$CH$_2$CH$_2$P), 38.09 (methyl), 129.58, 130.83, 131.70, 133.08, 134.22 (Phenyl). ^{31}P (DMSO-d_6): δ −11.49 (J = 3250 Hz). Colorless single crystals suitable for X-ray diffraction were obtained from CH_2Cl_2/Et_2O.

Preparation of $[(\mathrm{dppp})_2\mathrm{Pt}_2(\mu\text{-OH})(\mu\text{-NHNMe}_2)](\mathrm{OTf})_2$ 2. 1,1-Dimethylhydrazine (0.100 mL of a 0.40 M CH_2Cl_2 solution, 0.040 mmol) was added to a solution of $[(\mathrm{dppp})\mathrm{Pt}(\mu\text{-OH})]_2(\mathrm{OTf})_2$ (0.056 g, 0.040 mmol) in 1 mL of CH_2Cl_2. The yellow solution was stirred at ambient temperature for 2 h. Addition of Et_2O (10 mL) to the solution afforded a yellow precipitate. The precipitate was collected through filtration and washed twice with Et_2O (3 mL) to obtain a light yellow solid (0.053 g, 83%). Anal. Calcd (found) for $C_{58}H_{60}F_6N_2O_7P_4Pt_2S_2$: C, 43.83 (43.64); H, 3.80 (3.93); N, 1.76 (1.74). Mp: 220−222 °C. ^{1}H NMR (CD_2Cl_2): δ 1.86 (broad, 4H, PCH_2CH$_2$CH$_2$P cis to N or O), 1.98 (broad s, 6H, Me), 2.56 (broad, PCH$_2$CH$_2$CH_2P cis to N or O), 2.93 (broad, 4H, PCH$_2$CH_2CH$_2$P), 7.11−7.80 (m, 40H, phenyl). ^{13}C NMR (CD_2Cl_2): δ 15.46 (Me), 18.62, 22.78 (PCH$_2$CH$_2$CH$_2$P), 124.5, 128.7, 129.6, 130.0, 132.0, 132.2, 132.5, 133.5 (Phenyl). ^{31}P (CD_2Cl_2): δ −9.43 (J_{PP} = 28 Hz, J_{PPt} = 3604 Hz, P trans to O), −8.35 (J_{PP} = 28 Hz, J_{PPt} = 2596 Hz, P trans to N). IR: 3607 (OH), 3270 (NH). Yellow single crystals suitable for X-ray diffraction were obtained from CH_2Cl_2/Et_2O.

Reaction of 2 with Excess 1,1-Dimethylhydrazine. Compound **2** was dissolved in CH_2Cl_2 (1 mL) and treated with excess 1,1-dimethylhydrazine; the mixture was stirred overnight. Addition of Et_2O (10 mL) to the cloudy mixture afforded a white precipitate. The precipitate was collected through filtration and washed twice with Et_2O (3 mL) to obtain a light yellow solid (0.060 g, 85%). NMR and X-ray studies identified the yellow product as $(\mathrm{dppp})\mathrm{PtCl}_2$.[69]

Preparation of $[(\mathrm{dppp})_2\mathrm{Pt}_2(\mu\text{-OH})(\mu\text{-NHNHPh})](\mathrm{OTf})_2$ 3. Phenylhydrazine (0.100 mL of 0.40 M CH_2Cl_2 solution) was added to a solution of $[(\mathrm{dppp})\mathrm{Pt}(\mu\text{-OH})]_2(\mathrm{OTf})_2$ (0.056 g, 0.040 mmol) in 1 mL of CH_2Cl_2. The yellow solution was stirred at ambient temperature for 2 h. Addition of Et_2O (10 mL) to the solution afforded a yellow precipitate. The precipitate was collected through filtration and washed twice with Et_2O (3 mL) to obtain a light yellow solid (0.058 g, 86%). Anal. Calcd (found) for $C_{62}H_{60}F_6N_2O_7P_4Pt_2S_2{\cdot}0.5CH_2Cl_2$: C, 44.69 (44.14); H, 3.66 (3.73); N, 1.67 (1.75). Mp: 183−185 °C. ^{1}H NMR (CD_2Cl_2): δ −1.00 (s, 1H, OH or NH), 1.61−2.83 (broad m, 12H, PCH$_2$CH$_2$CH$_2$P), 3.23 (s, 1H, OH or NH), 4.12 (s, 1H, NH), 6.85−7.65 (m, 40H, phenyl). ^{13}C NMR (CD_2Cl_2): δ 18.63, 22.52 (PCH$_2$CH$_2$CH$_2$P), 114.5, 120.4, 124.2, 125.2, 127.1, 128.8, 129.4, 129.5, 130.1, 131.8, 132.2, 132.9 (Phenyl). ^{31}P (CD_2Cl_2): δ −9.37 (J_{PP} = 32 Hz, J_{PPt} = 3695 Hz, P trans to O), −6.45 (J_{PP} = 32 Hz, J_{PPt} = 2671 Hz, P trans to N). IR (KBr, cm^{-1}): 3563 (OH), 3306 (NH). Yellow single crystals suitable for X-ray diffraction were obtained from $ClCH_2CH_2Cl/{}^i\mathrm{Pr}_2O$.

Preparation of $[(\mathrm{dppp})\mathrm{Pt}(\mu\text{-NHNHPh})]_2(\mathrm{X})_2$ 4. X = BF_4. Phenylhydrazine (0.100 mL of 0.40 M CH_2Cl_2 solution) was added to a solution of $[(\mathrm{dppp})\mathrm{Pt}(\mu\text{-OH})]_2(\mathrm{BF}_4)_2$ (0.056 g, 0.040 mmol) in 1 mL of CH_2Cl_2. The yellow solution was stirred at ambient temperature for 2 h. Addition of Et_2O (10 mL) to the solution afforded a yellow precipitate. The precipitate was collected through filtration and washed twice with Et_2O (3 mL) to obtain a light yellow solid (0.053 g, 85%). Mp: 185−188 °C. ^{1}H NMR (250 MHz CD_2Cl_2): δ 1.82 (broad, 4H, PCH$_2$CH_2CH$_2$P), 2.55 (s, 2H, NH), 2.80−2.95 (broad, 8H, PCH$_2$CH$_2$CH_2P), 5.76 (d, 4H, J = 7.59 Hz, NH), 7.11−7.80 (m, 40H, phenyl). ^{13}C NMR (CD_2Cl_2): δ 17.78 (PCH$_2$CH$_2$CH$_2$P), 25.00 (PCH$_2$CH$_2$CH$_2$P), 119.2, 123.2, 129.0, 129.2, 130.3, 131.9, 133.0 133.4, (Phenyl). ^{31}P (CD_2Cl_2): δ −10.26 (J_{PPt} = 2860 Hz). IR: 3291, 3361 (NH). Yellow single crystals suitable for X-ray diffraction were obtained from $ClCH_2CH_2Cl/{}^t\mathrm{BuOMe}$. **X = OTf**. A procedure similar to that for the BF_4 salt yielded the OTf salt. Anal. Calcd (found) for $C_{68}H_{66}F_6N_4O_6P_4Pt_2S_2{\cdot}0.5CH_2Cl_2$: C, 46.48 (46.37); H, 3.82 (3.88); N, 3.16 (3.07). Spectroscopic properties were essentially identical to those of the BF_4 salt.

Reaction of NH_2NMe_2 with CH_2Cl_2. NH_2NMe_2 (0.060 g, 40 mmol) was dissolved in CH_2Cl_2 (5 mL). Colorless crystals of $[\mathrm{Me_2N(CH_2Cl)NH_2}]\mathrm{Cl}$ suitable for X-ray diffraction were collected and washed with CH_2Cl_2 (5 mL) and Et_2O (10 mL). Yield: 0.080 g (90%). Anal. Calcd (found) for $C_3H_{10}N_2Cl_2$: C, 24.85 (24.68); H, 6.95 (7.16); N, 19.32 (19.21). Mp: 118−120 °C. ^{1}H NMR (DMSO-d_6): δ 3.37 (s, 6H, Me), 5.52 (s, 2H, CH$_2$), 6.54 (s, 2H, NH$_2$). ^{13}C NMR (DMSO-d_6): δ 53.31 (Me), 71.87 (CH$_2$). IR: 3396, 3214 (NH). A similar procedure with $ClCH_2CH_2Cl$ yielded $[\mathrm{Me_2N(CH_2CH_2Cl)NH_2}]\mathrm{Cl}$.

Crystal Structure Analyses. Crystal data, reflection collection and processing parameters, and solution and refinement data are summarized in abbreviated Table 1. A full description is given in the Supporting Information. Crystals were grown as described in the syntheses given above. Crystals were mounted by pipetting crystals and mother liquor into a pool of heavy oil. A suitable crystal was selected and removed from the oil with a glass fiber. With the oil covered crystal adhering to the end of the glass fiber, the sample was transferred to an N_2 cold stream on the diffractometer, and data was collected at the temperatures indicated in Table 1.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of $[(\mathrm{dppp})_2\mathrm{Pt}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-MeNNMe})](\mathrm{BF}_4)_2$ **1**, $[(\mathrm{dppp})_2\mathrm{Pt}_2(\mu\text{−OH})(\mu\text{−NHNMe}_2)](\mathrm{OTf})_2$ **2**, $[(\mathrm{dppp})_2\mathrm{Pt}_2(\mu\text{-OH})(\mu\text{-NHNHPh})](\mathrm{OTf})_2$ **3**, $[(\mathrm{dppp})\mathrm{Pt}(\mu\text{-NHNHPh})]_2(\mathrm{BF}_4)_2$ **4**, and $[\mathrm{Me_2N(CH_2Cl)NH_2}]\mathrm{Cl}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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