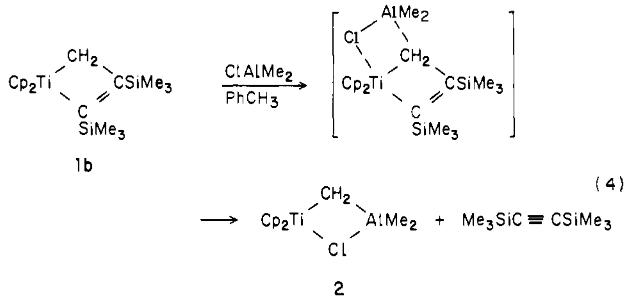
Table III. Promotion of CH_2 Exchange in the System[a] $Cp_2TiCH_2AlClMe_2 + {}^{13}CH_2{=}CMe_2 \rightleftharpoons Cp_2Ti^{13}CH_2AlClMe_2 + CH_2{=}CMe_2$

promoter[b]	CH_2 equilibration time at 25 °C
THF	<15 min
Et_2O	24 h
none	>18 days[c]

[a] Solutions containing 17 mg (0.060 mmol) of 2 in 0.15 mL of C_6D_6 were frozen and treated with 0.053 mmol of $^{13}CH_2{=}CMe_2$ and 0.053 mmol of the indicated ether. The mixtures were warmed to room temperature, and their ^1H NMR spectra were recorded immediately, and at intervals thereafter. Equilibration of methylene groups was judged to be complete when the concentrations of ^{13}C were the same in $CH_2{=}CMe_2$ and undecomposed $Cp_2TiCH_2AlClMe_2$. [b] Approximately two-thirds of the organometallic compound decomposed in the THF activated system. Decomposition in the diethyl ether system was ca. 12%. Decomposition was not detected in the ether-free system. We cannot eliminate the possibility that decomposition products are responsible for acceleration of the exchange rate. [c] The exchange was approximately 80% complete after 18 days.

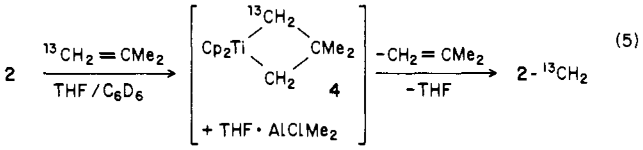
to yield the metallacyclobutane 4. Intermediate 4, as yet not isolated or detected, is also used in a scheme describing CH_2 exchange between $Cp_2TiCH_2AlClMe_2$ (2) and $CH_2{=}CMe_2$.[1] This exchange reaction yields the information that titanacyclobutene 1b is considerably more stable than titanacyclobutane 4.

The acetylene in 1b is also substituted by $ClAlMe_2$ when the aluminum reagent is supplied in the absence of THF (eq 4). Thus, the synthesis reaction (eq 1) and its reverse (eq 4) are markedly dependent on the solvent. Uncomplexed $ClAlMe_2$ competes effectively with $Me_3SiCCSiMe_3$ for Cp_2TiCH_2, but $THF{\cdot}AlClMe_2$ is not competitive.


(4)

In contrast to the elevated temperatures required for reactions of 1b with unsaturated hydrocarbons, the reaction with $ClAlMe_2$ occurs easily at room temperature. The facility of the aluminum reaction may be related to the ease of coordination of $ClAlMe_2$ with the titanacycle, with the result that the complex is activated for acetylene release. Two of the potential sites of aluminum attack are illustrated in eq 4, where $ClAlMe_2$ adds across the $TiCH_2$ group. A similar effect of $ClAlMe_2$ on a titanacyclobutane (olefin + 2) might limit its lifetime (see ref 1). In an early example of the effect of aluminum on a saturated titanacycle, Grubbs and Miyashita[13] found that $AlCl_3$ attacks $Cp_2\overline{TiCH_2(CH_2)_3CH_2}$ to produce butene and $Cp_2TiCH_2AlCl_3$.[2]

The $ClAlMe_2$ portion of 2 inhibits reactions of Cp_2TiCH_2 with acetylenes. One test for a similar $ClAlMe_2^-$ inhibition of olefin reactions is to examine the effect of bases on the rate of CH_2 exchange between 2 and an olefin. The olefin chosen for study is $^{13}CH_2{=}CMe_2$, which was found to exchange slowly with 2 in aromatic solvents.[1] We find that ethers markedly accelerate the rate of methylene exchange between 2 and $^{13}CH_2{=}CMe_2$ (Table III). With THF in the reaction mixture, the exchange (eq 5)[14] is faster by a factor of at least 10^3 compared with the rate for an unpromoted reaction. With 2 as an olefin metathesis catalyst[1] for methylene exchange between isobutene and methylenecyclohexane, rates of exchange are enhanced by THF.


(5)

The study of acetylene reactions of $Cp_2TiCH_2AlClMe_2$ (2) has assisted interpretation of the olefin chemistry of 2. The aluminum in 2 inhibits the reactivity of the complex with acetylenes and, we presume, with olefins. The reaction of titanacyclobutene 1b with $^{13}CH_2{=}CMe_2$ is a case of metal and olefin methylene exchange in an aluminum-free system. This information helps to refine the proposal that aluminum in $Cp_2TiCH_2AlClMe_2$ acts mainly to stabilize and deactivate the $TiCH_2$ group. It will be of interest to determine the effects of main-group alkyls on olefin metathesis catalysts generated from group 6 complexes.[15] Structures similar to 2 have been suggested for the catalyst made with WCl_6 and aluminum or zinc alkyls.[16]

The heterocycles $Cp_2\overline{TiCH_2CSiMe_3{=}CSiMe_3}$ and $Cp_2\overline{TiCH_2AlCl}Me_2$ preserve the highly reactive (and quite unstable) Cp_2TiCH_2[17] group for controlled reactions with olefins. An analogous system has been considered by Grubbs, who discussed the potential of metallacyclobutanes for storage and controlled release of reactive metal carbenes.[15a]

Acknowledgment. We thank D. K. Babcock and L. F. Lardear for skilled experimental assistance, Drs. W. Mahler and P. L. Watson for helpful interpretative comments, and Professors R. H. Grubbs, C. P. Casey, and J. J. Eisch for a series of useful discussions.

Supplementary Material Available: Positional and thermal parameters, least-squares planes, and structure amplitudes (14 pages). Ordering information is given on any current masthead page.

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[13] Grubbs, R. H.; Miyashita, A., personal communication.

[14] The interpretation of the reaction expressed in eq 5 requires that Cp_2TiCH_2 or titanacyclobutane 4 displaces THF from $THF{\cdot}AlClMe_2$. Studies of this type could provide an approximate idea of the basicity of Cp_2TiCH_2, relative to other bases, toward the Lewis acid $ClAlMe_2$.

[15] Catalysts prepared from group 6 compounds and main group alkyls are discussed in review articles: (a) Grubbs, R. H. *Prog. Inorg. Chem.* **1978**, *24*, 1-50. (b) Haines, R. J.; Leigh, G. J. *Chem. Soc. Rev.* **1975**, *4*, 155-188.

[16] Muetterties, E. L. *Inorg. Chem.* **1975**, *14*, 951-953.

[17] Erskine, G. J.; Hartgerink, J; Weinberg, E. L.; McCowan, J. D. *J. Organomet. Chem.* **1979**, *170*, 51-61.

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Received November 26, 1979

Linkage Isomerism of a Bidentate Triphosphate Ligand Having Six- or Eight-Membered Chelate Rings

Sir:

The importance of metal binding to phosphates in biological systems has led us to study the different possible modes of binding in metal–phosphate complexes by using substitution-inert metal ions in order that the configuration of the complexes is the same in the crystalline state as in solution. We have previously reported[1,2] on the β,γ-bidentate[3] coordination of triphosphate ion

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[1] Cornelius, R. D.; Hart, P. A.; Cleland, W. W. *Inorg. Chem.* **1977**, *16*, 2799-2805.

[2] (a) Merritt, E. A.; Sundaralingam, M.; Cornelius, R. D.; Cleland, W. W. *Biochemistry* **1978**, *17*, 3274-3278. (b) Merritt, E. A.; Sundaralingam, M. *Acta Crystallogr., Sect. B*, in press.

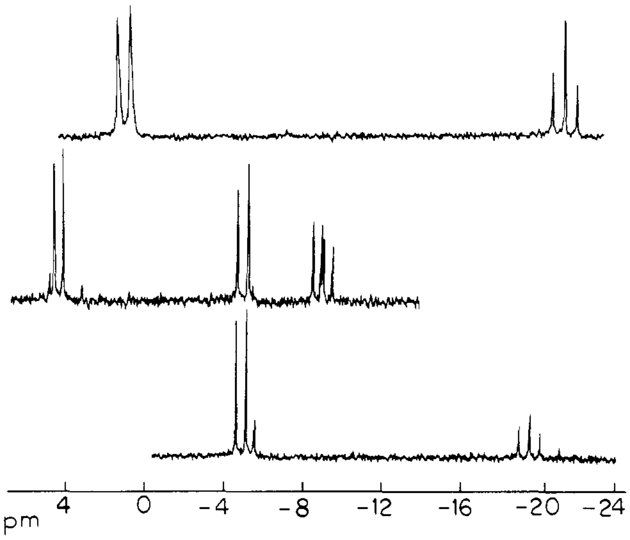

Figure 1. Phosphorus-31 NMR spectra at 36.4 MHz of (top) α,γ-[$Co(NH_3)_4P_3O_{10}$]$^{2-}$, (center) β,γ-[$Co(NH_3)_4P_3O_{10}$]$^{2-}$, and (bottom) $P_3O_{10}^{5-}$. The spectra were recorded at pH ≥8 to provide conditions which would deprotonate all of the phosphates. The small peak at −5.6 ppm in the spectrum of $P_3O_{10}^{5-}$ is due to an impurity of orthophosphate ion. Chemical shifts are relative to 85% H_3PO_4.

to cobalt(III) to form a six-membered chelate ring in $Co(NH_3)_4H_2P_3O_{10}\cdot H_2O$ [tetraammine(dihydrogen triphosphato)cobalt(III)]. We now describe a linkage isomer of this complex in which triphosphate ion is bidentate but coordinates through the α and γ phosphates to form an eight-membered chelate ring as revealed by phosphorus-31 NMR spectroscopy in solution and by X-ray crystallography in the solid state The rarity of linkage isomerism for bidentate ligands and the formation of an eight-membered chelate ring in a system in which a six-membered chelate ring is already known to form combine to make this α,γ-triphosphato complex a very interesting compound for detailed study.

Under the conditions previously given[1] for the formation of the β,γ isomer from [$Co(NH_3)_4CO_3$]NO_3 and $Na_5P_3O_{10}$, a small amount of the α,γ isomer is also formed. The anion-exchange chromatography at pH 5 used to separate the β,γ complex from other reaction products also separates the two isomers of $Co(NH_3)_4H_2P_3O_{10}$ when a longer anion-exchange column is used. The pK at 5.8 for the uncoordinated terminal phosphate of the β,γ isomer[4] gives this isomer a lower negative charge at pH 5 and causes it to move down the column slightly faster than the α,γ isomer. The overall yield of the α,γ complex is 2%.

Phosphorus-31 NMR spectroscopy has proved to be a powerful tool for determining the mode of binding of phosphates in cobalt(III) complexes. Coordination chemical shifts in the range of 7–14 ppm downfield have been observed by several workers[1,4–6] upon coordination of phosphates to one cobalt(III) ion. Even higher shifts have been observed upon coordination of a second cobalt(III) ion to a single phosphate ligand.[6] Figure 1 presents the phosphorus-31 NMR spectrum of the α,γ complex (top) along with the spectra of the β,γ complex (center) and the free triphosphate ion (bottom). The spectrum of the β,γ complex shows that the position of one terminal phosphorus atom (the doublet at −5 ppm) is hardly shifted from the position for the free ligand while the other terminal phosphorus atom (the doublet at 4 ppm) and the center phosphorus atom (the double doublet) are each shifted downfield by 10 ppm from the corresponding peaks for the free ligand. The spectrum of the α,γ complex shows that both terminal phosphorus atoms (the doublet) are shifted downfield compared to the free triphosphate ion while the middle phosphorus atom (the triplet) is hardly shifted from the position in the free ligand. These shifts are consistent with the coordination of only the terminal phosphates to form an eight-membered chelate ring. A similar, but poorly resolved, spectrum has been reported for a bis(ethylenediamine) complex of cobalt(III).[5b]

Table I. Selected Bond Lengths and Angles for α,γ-$Co(NH_3)_4H_2P_3O_{10}$

bond lengths, Å		bond angles, deg	
Co–O1	1.933 (2)	Co–O1–P1	150.9 (2)
O1–P1	1.488 (3)	O1–P1–O4	109.7 (2)
P1–O4	1.592 (3)	P1–O4–P2	133.0 (2)
O4–P2	1.613 (3)	O4–P2–O7	102.2 (2)
P2–O7	1.609 (3)	P2–O7–P3	129.7 (2)
O7–P3	1.603 (3)	O7–P3–O10	111.4 (2)
P3–O10	1.490 (3)	P3–O10–Co	140.1 (2)
O10–Co	1.921 (2)	O10–Co–O1	94.6 (2)

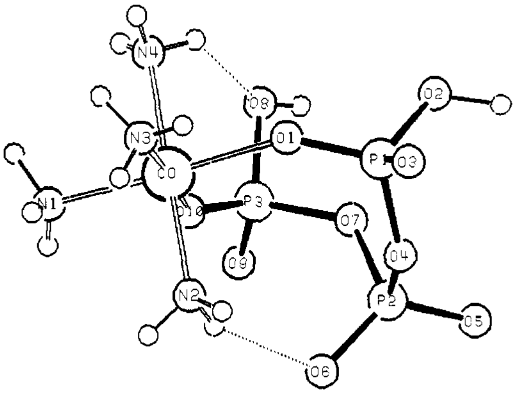

Figure 2. The molecular structure of α,γ-$Co(NH_3)_4H_2P_3O_{10}$, showing the boat configuration of the eight-membered chelate ring.

The crystallization procedure[1] used for the preparation yields analytically pure but highly twinned crystals. The crystals used for the structure determination were prepared by dissolving 2 mg of the crude crystals in 2 mL of water by the dropwise addition of 1 M NaOH. The pH was lowered to 3.3 by the addition of 1 M HCl, and 1 mL of ethanol was added. One week of storage at 4 °C produced well-formed crystals belonging to the monoclinic space group $P2_1/n$ with unit-cell parameters a = 7.234 (5), b = 14.107 (1), c = 12.113 (1) Å; β = 92.909 (5)°; Z = 4; R_f = 0.052 for all 2608 unique reflections, and R_f = 0.046 for 2371 reflections with $F_o > 3\sigma(F_o)$. Selected bond lengths and angles are given in Table I.

The molecular structure[7] is shown in Figure 2 in an orientation which emphasizes the boat conformation of the eight-membered ring. In this conformation, the chelate ring is stabilized by two interligand hydrogen bonds involving N2–O6 and N4–O8 which are on opposite sides of the chelate ring. These intramolecular hydrogen bonds involve only the β and γ phosphates. The O–Co–O angle is 94.6 (2)°, 2.1° larger than the 92.5 (1)° found in the β,γ isomer, while the ligand bite is essentially the same as in the β,γ isomer [2.831 (4) Å vs. 2.818 (8) Å, respectively]. Although these differences can be attributed to the greater strain inherent in the eight-membered ring, the small magnitude of the differences attests to the flexibility of the triphosphate chain. That flexibility is shown by the marked difference between the two isomers in the chelate ring bond angles. The bond angles at the three-ring oxygen atoms in the six-membered ring fall within the range 128.4 (3)° to 129.8 (3)° while for the eight-membered ring

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(3) This complex, in which the center phosphate group and one terminal phosphate group are coordinated, is labeled β,γ by analogy with the ATP complex from which crystals for the structure determination were prepared (ref 1 and 2). We have also reported the α,β,γ-tridentate binding of triphosphate ion to form two six-membered chelate rings in $Co(NH_3)_3H_2P_3O_{10}$. See ref 1 and Merritt, E. A.; Sundaralingam, M. August 1977 Meeting of the American Crystallographic Association; Abstr. F7.

(4) Cornelius, R. D. *Inorg. Chem.* **1980**, *19*, 1286–1290.

(5) (a) Seel, F.; Gohnstedt, G. *Z. Anorg. Allg. Chem.* **1977**, *435*, 257–267. (b) *Ibid.* **1978**, *441*, 237–244.

(6) Hubner, P. W. A.; Milburn, R. M. *Inorg. Chem.* **1980**, *19*, 1267–1272.

(7) Details of the structure have been submitted to *Acta Crystallogr., Sect. B* for publication. Positional and isotropic thermal parameters are given as Table II in Supplementary Material.

the bond angles at the four-ring oxygen atoms vary from 130.0 (2)° up to 150.9 (2)°. The formation of the eight-membered ring also constrains the triphosphate chain to be in a much more highly folded configuration than in the β,γ complex or in other crystal structures of the triphosphate ion. The α,γ complex exhibits a PPP angle of 86.0° and a P1–P3 distance of 3.987 Å as compared to 116.1° and 4.905 Å for the β,γ complex.

Acknowledgment. We are grateful to Professors Delbert Mueller at Kansas State University and P. A. Hart at the University of Wisconsin—Madison for recording the NMR spectra. This research was supported by Research Corporation, by the National Science Foundation (Grant CHE-7809301), and by the National Institutes of Health (Grant GM-17378).

Supplementary Material Available: Fractional coordinates and thermal parameters (Table II) of α,γ-$Co(NH_3)_4H_2P_3O_{10}\cdot H_2O$ (1 page). Ordering information is given on any current masthead page.

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Reactions of Coordinated Dinitrogen. 8.[1] Formation of Ammonia by Protonation of a Molybdenum–Dinitrogen Complex and Isolation and Characterization of the Molybdenum-Containing Product

Sir:

The conversion of metal-bound dinitrogen, N_2, into ammonia by protonolysis in high stoichiometric yield was first reported in 1975,[2,3] and an example is shown in eq 1, where L = PMe_2Ph or

$$W(N_2)_2L_4 \xrightarrow[\text{MeOH, 20 °C}]{H_2SO_4} 2[NH_4^+] + N_2 + 4[HL][HSO_4] + [\text{W(VI) oxide?}] \quad (1)$$

$PMePh_2$. A similar reaction occurred with the molybdenum analogues although the yield of ammonia was lower than for the corresponding tungsten complexes. By variation of the protic acid and the solvent, it is possible to produce hydrazine as well as ammonia.[5]

In this communication, we present our recent results concerning the conversion of coordinated N_2 into ammonia, which differ in a number of significant ways from work previously reported.[2-5] We have successfully accomplished the first reported conversion of metal-coordinated dinitrogen into ammonia in which the fate of the metal has been determined. This reaction is shown in eq 2, where triphos = $PhP(CH_2CH_2PPh_2)_2$ and L = PPh_3. Complex

$$\underset{\mathbf{1}}{2Mo(N_2)_2(triphos)(L)} + 8HBr \rightarrow 2NH_4Br + 2MoBr_3(triphos) + 3N_2 + 2L \quad (2)$$

1,[1] a new subclass of bis(dinitrogen) complexes of molybdenum, reacted in tetrahydrofuran (THF) solution with anhydrous hydrogen bromide to produce ammonium bromide. No hydrazine or hydrazinium bromide was detected among the reaction products.[6] Ammonium bromide was detected by infrared spectroscopy among the reaction products after solvent and excess HBr had been removed in vacuo. The yield of ammonia was determined quantitatively by the indophenol method after either aqueous, nonaqueous (ethanol), or two-phase (dichloromethane–water) extraction of ammonium bromide from the residue.

There are a number of significant features of this reaction that deserve mention. (i) The six electrons that are required for the conversion of N_2 into $2NH_3$ came from $2Mo(0) \rightarrow 2Mo(III) + 6e^-$. In previous work, it has been proposed that the six electrons necessary for the reduction of N_2 to ammonia came from $M(0) \rightarrow M(VI) + 6e^-$.[2] (ii) This was the first time that the metal-containing (molybdenum in this case) product has been characterized after ammonia formation; $MoBr_3$(triphos) was isolated in >90% yield.[7] (iii) Base distillation *was not required* in order to liberate (or produce) ammonia from the reaction products. This is to be contrasted with other work where base distillation was required either to separate ammonia from the reaction products or to assist in the final step(s) of the conversion of metal-bound N_2 into ammonia.[2,5] (iv) The isolated molybdenum-containing product was the precursor for the preparation of the bis(dinitrogen) complex **1**.[8]

In a typical reaction carried out on a vacuum line, THF (10 mL) and anhydrous HBr (3.6 mmol) were condensed into a round-bottomed flask (25 mL) cooled to −196 °C, containing complex **1** (0.2 mmol) and a small magnetic stirring bar. When the mixture was warmed, the solvent melted to give a bright orange suspension. Just above 0 °C, a gas was observed to bubble from the suspension, which eventually became a yellow homogeneous solution when gas evolution had ceased. At this time, between 0.9 and 1.0 mol of N_2 per molybdenum atom had been evolved as determined by Toepler pump measurements.[9] A further 0.4–0.5 mol of N_2 per molybdenum atom was evolved when the solution was allowed to stir for 24–36 h at room temperature. By this time, both NH_4Br and $MoBr_3$(triphos) had precipitated from solution. The total amount of N_2 evolved ranged between 1.3 and 1.5 mol. Solvent was removed and the residue extracted with a mixture of dichloromethane and water. The dichloromethane layer was separated and extracted with more water. The combined aqueous fractions were made up to a known volume and analyzed for ammonia by the indophenol method. Generally, yields of ammonia approached or slightly exceeded 0.7 mol per atom of molybdenum. The molybdenum-containing product slowly decomposed during the dichloromethane–water extraction step. Isolation of pure $MoBr_3$(triphos) was carried out in a separate experiment in which only N_2 evolution was measured. All volatiles were removed from the reaction vessel, and the resulting yellow solid was washed with ethanol and dried. Its identity was confirmed by elemental analysis.[7]

The reaction appeared to proceed in two steps. The first step was the relatively rapid loss of 1 mol of N_2. This is very similar to the reported reactions of excess HBr with $M(N_2)_2(dppe)_2$ and $M(N_2)_2(PMe_2Ph)_4$ (where M = Mo or W and dppe = $Ph_2PCH_2CH_2PPh_2$) to form the corresponding hydrazido(2−) complexes $[MBr(NNH_2)(dppe)_2]Br$ and $MBr_2(NNH_2)(PMe_2Ph)_3$, respectively, with the rapid loss of 1 mol of N_2.[10]

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(1) Part 7: George, T. A.; Kovar, R. A. *Inorg. Chem.*, submitted for publication.

(2) Chatt, J.; Pearman, A. J.; Richards, R. L. *Nature* (*London*) **1975**, *253*, 39–40. *J Chem. Soc., Dalton Trans.* **1977**, 1852–1860.

(3) Many other reports of the formation of ammonia from dinitrogen in the presence of metal ions and reducing agents have appeared. Most of the work has been critically analyzed and published in a recent review article.[4]

(4) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589–625.

(5) Takahasti, T.; Mizobe, Y.; Sato, M.; Uchida, Y.; Hidai, M. *J. Am. Chem. Soc.* **1979**, *101*, 3405–3407.

(6) Analysis for hydrazine was carried out by the *p*-(dimethylamino)-benzaldehyde method: Watt, G.; Chrisp, J. D. *Anal. Chem.* **1952**, *24*, 2006–2008.

(7) Anal. Calcd for $MoBr_3$(triphos), $C_{34}H_{33}Br_3MoP_3$: C, 46.93; H, 3.82; Br, 27.55. Found: C, 47.0; H, 3.78; Br, 27.76.

(8) Complex **1** was prepared by the reduction of MoX_3(triphos) (X = Cl or Br) with sodium amalgam in THF under an atmosphere of dinitrogen with PPh_3 (1.1 mol) present. [1]Anal. Calcd for $Mo(N_2)_2(triphos)(PPh_3)\cdot{}^1/_2THF$, $C_{54}H_{52}MoN_4O_{1/2}P_4$: C, 65.9; H, 5.28; N, 5.69. Found: C, 64.8; H, 5.30; N, 5.70. IR (ν_{NN}) (KBr) 1955 cm^{-1}.

(9) Gases were analyzed by mass spectroscopy and results compared with N_2–H_2 mixtures of known different ratios. The maximum amount of dihydrogen found in the dinitrogen gas never exceeded 0.1% of the total amount of gas evolved.

(10) Chatt, J.; Heath, G. A.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1974**, 2074–2082.

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