

Preparation, Characterization, and Reactivity of Dinitrogen Molybdenum Complexes with Bis(diphenylphosphino)amine Derivative Ligands that Form a Unique 4-Membered P–N–P Chelate Ring

Takahiko Ogawa,[†] Yuji Kajita,[†] Yuko Wasada-Tsutsui,[†] Hiroaki Wasada,[‡] and Hideki Masuda^{*,†}

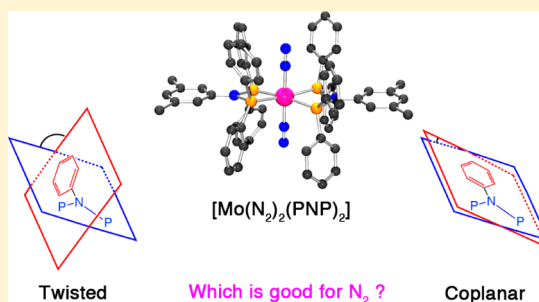
[†]Department of Frontier Materials, Graduate School of Engineering, Nagoya Institute of Technology Gokiso, Showa, Nagoya 466-8555, Japan

[‡]Faculty of Regional Studies, Gifu University, Gifu 501-1193, Japan

S Supporting Information

ABSTRACT: Five dinitrogen–molybdenum complexes bearing bis-(diphenylphosphino)amine derivative ligands (L^R) that form a unique 4-membered P–N–P chelate ring, $trans-[Mo(N_2)_2(L^R)_2]$ (2^R : R = Ph, Xy, *p*-MeOPh, 3,5-*i*Pr₂Ph, *i*Pr), were prepared for the purpose of binding a dinitrogen molecule. The corresponding two dichloride–molybdenum complexes, $trans-[MoCl_2(L^R)_2]$ (1^R : R = Ph, Xy), were also prepared as comparisons. FT-IR spectra of 2^R were measured and compared the $\nu(N\equiv N)$ values. Moreover, X-ray crystal structure determination of 1^R (R = Ph, Xy) and 2^R (R = Xy, 3,5-*i*Pr₂Ph) is performed. These experimental results indicated that the coordinated dinitrogen molecule gets easily influenced by the N-substituent of diphosphinoamine ligand.

In addition, to investigate the effect of the properties of the diphosphinoamine ligand for the dinitrogen molybdenum complexes, we performed DFT calculations that focused on the difference of N-substituent, the dihedral angle between P–N–P plane and N-substituent aryl group, and the P–N–P bite angle. This calculation revealed that the competition between the back-donation from metal to dinitrogen and that from metal to ligand was affected by P–N–P bite angle and the dihedral angle of N-substituent of ligand. In order to examine the reactivity with respect to conversion of dinitrogen to ammonia, protonation and trimethylsilylation reactions of the coordinated dinitrogens were carried out for 2^R .



INTRODUCTION

It is well-known that nitrogen (N) is an essential atom in biology. This atom also has important applications in production of fertilizers, and energy sources, as well as commercial chemical products and pharmaceuticals. Today, we depend on the Haber–Bosch process as a source of nitrogen. The Haber–Bosch process can reduce dinitrogen (N₂) to ammonia under high temperature and high pressure in the presence of Fe/Ru catalysts. However, this process requires a large amount of energy and dihydrogen generated from fossil fuels.¹ Development of dinitrogen fixation systems which function effectively under ambient reaction conditions is one of the most important research areas in chemical research and development.² Since the first example of a transition metal–dinitrogen complex, $[Ru(N_2)(NH_3)_5]^{2+}$, was reported by Allen and Senoff in 1965,³ various transition metal–dinitrogen complexes have been synthesized to study its reaction mechanism in efforts to develop dinitrogen fixation systems.⁴ In 1969, Hidai and co-workers reported on a group 6 metal dinitrogen complex, $trans-[Mo(N_2)_2(dppe)_2]$ (dppe = 1,1'-bis(diphenylphosphino)ethane).⁵ In 1975, Chatt and co-workers succeeded in obtaining stoichiometric reduction of dinitrogen to ammonia by protonation of molybdenum- and

tungsten-dinitrogen complexes, $[M(N_2)_2(PR_3)_4]$ (M = Mo, W, R = alkyl, aryl), and further investigated various transition metal phosphorus dinitrogen complexes.⁶ In 1997, Fryzuk and co-workers studied the reaction of a side-on bound dinitrogen zirconium complex, $\{[PhP(CH_2SiMe_2NSiMe_2CH_2)_2PPh]_2Zr\}_2(\mu-\eta^2-N_2)$, with dihydrogen to obtain the complex $\{[PhP(CH_2SiMe_2NSiMe_2CH_2)_2PPh]_2Zr\}_2(\mu-\eta^2-N_2H)(\mu-H)$.⁷ For metal complexes without phosphine ligands, many dinitrogen complexes with various metals and various ligands have been synthesized and studied.⁸ In 2003, Schrock and Yandulov succeeded in direct catalytic conversion of dinitrogen to ammonia using a molybdenum–dinitrogen complex bearing triamidoamine as the supporting ligand.⁹ In 2004, Chirik and co-workers reported direct generation of ammonia from dinitrogen and dihydrogen using a dinuclear zirconium complex with a cyclopentadienyl derivative.¹⁰ Despite the many studies of metal complexes with amido or cyclopentadienyl ligands, there are few examples of catalytic reduction of dinitrogen using molybdenum(0)–phosphine complexes.¹¹ Recently, Nishibayashi and co-workers reported

Received: July 19, 2012

Published: December 11, 2012



high-performance catalytic reduction of dinitrogen to ammonia using a molybdenum(0)–phosphine complex bearing PNP-type pincer ligands.¹² Extensive studies have been carried out over the past 40 years. However, there have been few examples of complexes for which the reduction mechanism has been rationally demonstrated by isolating the fully characterized intermediate stages. Therefore, molybdenum– and tungsten–phosphine dinitrogen complexes remain the subject of aggressive research with the objective of clarifying the reaction mechanism and developing high-performance dinitrogen reduction catalysts.¹³

For the Chatt type Mo/W–N₂ complexes, Tuczuk and co-workers investigated these complexes using spectroscopic and theoretical methods and evaluated the mechanism of dinitrogen reduction.¹⁴ On the basis of these studies, we noted the bite angle of phosphine ligands. Because bite angle is a very important factor to determine the properties of metal complexes, correlation between bite angle of diphosphine ligands and reactivity of complexes was investigated a lot.¹⁵ Although there are many examples of *trans*-[M(N₂)₂(P₄)] (P₄ = mono-, bi-, or tridentate phosphine ligand), these complexes have five- or six-membered chelate ring and similar bite angle (P–M–P angle is around 90°). This means that these complexes have relatively flexible phosphorus atoms which can locate a vertex of the regular octahedron. However, examples of Mo/W–N₂ complexes which have rigid phosphorus atoms and small bite angles (structure completely different from the regular octahedron) are very limited.¹⁶ We decided to use a ligand system that has a small bite angle (P–M–P angle) and 4-membered chelate ring for N₂ chemistry. We therefore focused on molybdenum diphosphinoamine dinitrogen complexes. It was previously reported that Cr(III) complexes with diphosphinoamine ligands have the potential to catalyze more highly selective ethylene polymerizations relative to similar complexes with diphenylphosphinoethane and *N,N'*-diphenylphosphinohydrazine ligands.¹⁷ The phosphinoamine ligands have been used widely because they can be prepared easily, can exchange N-substituent easily, and can provide small bite angle structure.^{18,19} Therefore, systematic study can be performed.²⁰ The molybdenum atom is occasionally employed for dinitrogen fixation chemistry and plays a key role in the active site of nitrogenase enzymes.²¹

Herein, we report the synthesis and characterization of molybdenum(0)–dinitrogen complexes supported by bis-(diphenylphosphino)amine ligands that form a unique 4-membered chelate ring, and discuss the dinitrogen activation factor by comparing the influences on the coordinated dinitrogen by N-substituents of diphosphinoamine ligands on the basis of structural and IR spectroscopic studies as well as from the viewpoint of theoretical calculations and reactions involving protonation and silylation.

EXPERIMENTAL SECTION

General Methods. All manipulations were carried out under an atmosphere of purified argon or dinitrogen gas in a mBRAUN MB 150B-G glovebox or by standard Schlenk techniques. ¹H NMR (300 MHz Varian, 600 MHz Bruker) and ³¹P{¹H} NMR (121 MHz Varian, 243 MHz Bruker) spectra were measured on a Varian Mercury 300 spectrometer or a Bruker Avance 600 spectrometer, and ¹H chemical shifts were estimated relative to TMS as an internal standard. ³¹P chemical shifts are quoted relative to an external standard of 85% H₃PO₄. ¹⁵N{¹H} NMR (61 MHz) spectra were measured on a Bruker Avance 600 spectrometer, and ¹⁵N chemical shifts are quoted relative to an external standard of nitromethane (CH₃NO₂). Fourier transform

infrared (FT-IR) spectra of solid compounds were taken as KBr pellets using a JASCO FT/IR-410 spectrophotometer. Elemental analyses were obtained with a Perkin-Elmer CHN-900 elemental analyzer. Gas chromatography/mass spectrometry (GC/MS) measurements were carried out on a SHIMADZU GCMS-QP2010 system.

X-ray Crystallography. Single crystals of **1^{Ph}**, **1^{Xy}**, **2^{Xy}**, and **2^{3,5iPrPh}** suitable for X-ray diffraction analyses were obtained from THF solutions after standing for a few days under an N₂ atmosphere at 238 K. A crystal was mounted on a glass fiber, and diffraction data were collected on a Rigaku/MSC Mercury CCD using graphite monochromated Mo K α radiation at 173 K. The structures were solved by a combination of direct methods (SIR 92 or SIR2004) and Fourier techniques. All non-hydrogen atoms except for some of the solvated molecules were refined anisotropically. Hydrogen atoms were refined using the riding model. The Sheldrick weighting scheme was employed. Plots of $\sum w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $\sin \theta/\lambda$, and various classes of indices showed no unusual trends. Neutral atomic scattering factors were obtained from International Tables for X-ray Crystallography Vol. IV.²² Anomalous dispersion terms were included in F_{calc} ²³ and the values for $\Delta f'$ and $\Delta f''$ were obtained from the International Tables for X-ray Crystallography Vol. C.²⁴ The values of the mass attenuation coefficients are those of the International Tables for X-ray Crystallography Vol. C.²⁵ All calculations were performed using the crystallographic software package, CrystalStructure.²⁶ A summary of crystallographic data is provided in the Supporting Information (Table S1).

Materials. The molybdenum trichloride tris(tetrahydrofuran) complex, [MoCl₃(THF)₃], was synthesized according to the literature procedure.²⁷ 3,5-Diisopropylaniline was synthesized from 2,6-diisopropylaniline according to the literature procedures.²⁸ Other reagents were employed in the commercially available forms. All anhydrous solvents were purchased from Sigma-Aldrich. For degassing, these solvents were bubbled with N₂.

Syntheses of Diphenylphosphinoamine Ligands (L^R: R = Ph, Xy, *p*-MeOph, *i*Pr, *p*-CNPh, H). The diphenylphosphinoamine ligands except **L^{3,5iPrPh} were prepared by a modification of literature procedures.^{19b,29–31} A flask equipped with an additional funnel was charged with a THF solution of 1 equiv of primary amine and 2 equiv of triethylamine. The solution was cooled to 0 °C. The additional funnel was charged with a THF solution of 2 equiv of chlorodiphenylphosphine, and the resulting solution was slowly added to the amine solution. The mixture was stirred at room temperature overnight. The triethylammonium salt was then separated by filtration, and the solvent was removed under vacuum. The residue was dissolved in a small amount of dichloromethane and precipitated with *n*-hexane, to produce a white powder. In the case of L^H, 1,1,1,3,3,3-hexamethyldisilazane was used instead of primary amine.³⁰ All compounds were characterized by ¹H NMR, ³¹P{¹H} NMR, and FT-IR spectroscopies.**

Synthesis of *N,N*-Bis(diphenylphosphino)-3,5-diisopropylaniline (L^{3,5iPrPh}). The novel ligand **L^{3,5iPrPh}** was prepared from 3,5-diisopropylaniline instead of primary amine,²⁸ according to the same procedure described above (white powder, 1.52 g, yield 82.2%).

¹H NMR (600 MHz, δ /ppm from TMS in CDCl₃): δ 0.87 [d, 12H, CH(CH₃)₂], 2.51 [sep, 2H, CH(CH₃)₂], 6.17 [s, 2H, *o*-H-PhN], 6.64 [s, 1H, *p*-H-PhN], 7.25–7.37 [m, 20H, *H*-Ph₂P]. ³¹P{¹H} NMR (243 MHz, δ /ppm from H₃PO₄ in CDCl₃): δ 69.5. FT-IR (KBr, cm^{−1}): ν 3050 (aromatic C–H), 2956 (aliphatic C–H), 1309 (aromatic C–N), 881 (P–N), δ 1435, 1430 (aliphatic C–H), 748, 697 (aromatic C–H). Anal. Calcd for C₃₆H₃₇NP₂: C, 79.24; H, 6.83; N, 2.57. Found: C, 79.39; H, 6.94; N, 2.45.

Synthesis of *trans*-[MoCl₂(L^R)₂] (L^R: R = Ph (1^{Ph}), Xy (1^{Xy})). A mixture of 2 equiv of L^R (R = Ph, Xy) and 1 equiv of [MoCl₃(THF)₃] in toluene was added to 1 equiv of potassium graphite. The mixture was stirred under an argon atmosphere at room temperature for 24 h. After concentration *in vacuo*, the residue was extracted with THF. Recrystallization at −35 °C gave red-orange crystals of **1^R** (R = Ph (1^{Ph}: yield 14.5%), Xy (1^{Xy}: 39.2%)).

Data for **1^{Ph}** follow. FT-IR (KBr, cm⁻¹): ν 1313 (aromatic C–N), 862 (P–N). Anal. Calcd for C₆₀H₅₀Cl₂MoN₂P₄: C, 66.13; H, 4.62; N, 2.57. Found: C, 65.85; H, 4.59; N, 2.58. Data for **1^{Xy}** follow. FT-IR (KBr, cm⁻¹): ν 1313 (aromatic C–N), 862 (P–N). Anal. Calcd for C₆₂H₅₄Cl₂MoN₂P₄·1.5THF: C, 67.04; H, 5.63; N, 2.23. Found: C, 66.42; H, 5.73; N, 2.23.

Synthesis of trans-[Mo(N₂)₂(L^R)₂] (**2^R**: R = Ph (**2^{Ph}**), Xy (**2^{Xy}**), *p*-MeOPh (**2^{MeOPh}**), *i*Pr (**2^{iPr}**), 3,5-*i*Pr₂Ph (**2^{3,5iPrPh}**)) and trans-[Mo-(¹⁵N₂)₂(L^R)₂] (**3^R**: R = Ph (**3^{Ph}**), Xy (**3^{Xy}**), 3,5-*i*Pr₂Ph (**3^{3,5iPrPh}**)). An excess amount of magnesium turnings was added to a mixture of 2 equiv of L^R and 1 equiv of [MoCl₃(THF)₃] in toluene. The mixture was stirred under dinitrogen (**2^R**) or a ¹⁵N-enriched dinitrogen (**3^R**) atmosphere at room temperature for 24 h. Removal of unreacted magnesium and filtration afforded a residue. Washing with methanol and *n*-hexane gave a red-orange powder of **2^R** and **3^R** (yields: **2^{Ph}**, 34.5%; **2^{MeOPh}**, 23.9%; **2^{iPr}**, 13.6%; **3^{Ph}**, 34.5%; **3^{Xy}**, 25.1%; **3^{3,5iPrPh}**, 47.6%). The solubility of **2^R** is extremely low except for **2^{Xy}** and **2^{3,5iPrPh}**. Therefore, it is difficult to dissolve these compounds in a number of solvents. The complexes **2^{Xy}** and **2^{3,5iPrPh}** were dissolved in THF and were recrystallized at –35 °C to give red-orange crystals (yields: **2^{Xy}**, 12.0%; **2^{3,5iPrPh}**, 49.7%).

FT-IR (KBr, cm⁻¹): ν 1990 (**2^{Ph}**), 2011 (**2^{Xy}**), 1995 (**2^{MeOPh}**), 1975 (**2^{iPr}**), 2014 (**2^{3,5iPrPh}**), 1923 (**3^{Ph}**), 1934 (**3^{Xy}**), 1947 (**3^{3,5iPrPh}**) (asymmetric N₂). Anal. Calcd for C₆₄H₅₈MoN₆P₄·THF: C, 67.88; H, 5.53; N, 6.99. Found: C, 66.88; H, 5.53; N, 6.82. (**2^{Xy}**). Anal. Calcd for C₇₂H₇₄MoN₆P₄·2THF: C, 69.25; H, 6.54; N, 6.06. Found: C, 69.45; H, 5.23; N, 6.20. (**2^{3,5iPrPh}**). ¹H NMR (300 MHz, δ /ppm from TMS in THF-*d*₈): δ 1.86 (s, 12H, CH₃), 6.43 (s, 4H, *o*-H-PhN), 6.51 (s, 2H, *p*-H-PhN), 7.10–7.27 (m, 40H, *H*-Ph₂P) (**2^{Xy}**), 0.84 (d, 24H, CH(CH₃)₂), 2.51 (sep, 4H, CH(CH₃)₂), 6.57 (s, 2H, *p*-H-PhN), 6.62 (s, 4H, *o*-H-PhN), 7.15–7.36 (m, 40H, *H*-Ph₂P). ¹⁵N{¹H} NMR (60.8 MHz, δ /ppm from CH₃NO₂ in THF-*d*₈): δ –46.34 (¹⁵N_a), –45.99 (¹⁵N_β) (**3^{Xy}**), –46.47 (¹⁵N_a), –46.03 (¹⁵N_β) (**3^{3,5iPrPh}**).

Reaction with HOTf. The dinitrogen complex **2^{3,5iPrPh}** (70.0 mg, 0.0563 mmol) was treated with HOTf (16.9 mg, 0.113 mmol) in THF (10 mL). After 1 h, the solution was concentrated and measured by FT-IR spectroscopy.

Reaction with H₂SO₄. To a THF (5 mL) suspension of a complex was added H₂SO₄. After 24 h of stirring at room temperature, ammonia was base distilled and quantified by the indophenol method.

Silylation of **2^R.** The dinitrogen complex **2^R** (10.0 mg) was treated with trimethylsilyl chloride (856 mg, 7.88 mmol) and sodium metal (50.0 mg, 2.17 mmol) in THF (5 mL). After 24 h, the solution was quantified by GC/MS.

COMPUTATIONAL DETAILS

Geometry optimizations of dinitrogen complexes, **2^{Ph}**, **2^{Xy}**, and **2^{3,5iPrPh}**, and dinitrogen methyl-substituted complex **2(PMe₂)^{Ph}** where all the phenyl groups in diphenylphosphino groups of **2^{Ph}** were substituted by methyl groups were performed at the B3LYP level.³² We used Stuttgart/Dresden ECP and basis set on Mo^{33a} together with 6-31+G(d) on P and N,^{33b,c} 6-31G(d)^{33d} on N-substituted aryl carbon and *ipso*-carbons attached to phosphorus, and 6-31G on the remaining atoms.^{33e} The results of frequency calculations at the same level confirmed that each of the optimized structures are at a minimum on the potential energy surface.

We calculated natural atomic charges and atom–atom overlap-weighted natural atomic orbital (NAO) bond orders^{34a,b} of the dinitrogen complexes and the methyl-substituted complex. We also calculated differential density $\Delta\rho(\mathbf{r})$ (eq 1) in order to investigate the change in electron density accompanied by coordination of dinitrogen molecules to the molybdenum complex.

$$\Delta\rho(\mathbf{r}) = \rho(\mathbf{r}, \text{dinitrogen complex}) - \{\rho(\mathbf{r}, \text{complex without dinitrogen}) + \rho(\mathbf{r}, \text{dinitrogen})\} \quad (1)$$

Here $\rho(\mathbf{r}, X)$ represents electron density of species X at a point $\mathbf{r}$. The values of $\rho(\mathbf{r}, \text{complex without dinitrogen})$ and $\rho(\mathbf{r}, \text{bisdinitrogen})$ were calculated using atomic coordinates fixed to the optimized

structure of the bisdinitrogen complex. We employed $\rho(\mathbf{r}, \text{complex without dinitrogen})$ of $S = 1$ state which has lower energy than that of the $S = 0$ state.

$\Delta\rho$ condensed to atoms and bonds, $\Delta\rho_{\text{atom}}$ (eq 2) and $\Delta\rho_{\text{BO}}$ (eq 3), respectively, were computed by carrying out natural population analysis.

$$\Delta\rho_{\text{atom}}(\text{A}) = +\rho_{\text{atom}}(\text{A}, \text{bisdinitrogen complex}) - \{\rho_{\text{atom}}(\text{A}, \text{complex without dinitrogen}) + \rho_{\text{atom}}(\text{A}, \text{bisdinitrogen})\} \quad (2)$$

$$\Delta\rho_{\text{BO}}(\text{A–B}) = -\rho_{\text{BO}}(\text{A–B}, \text{bisdinitrogen complex}) + \{\rho_{\text{BO}}(\text{A–B}, \text{complex without dinitrogen}) + \rho_{\text{BO}}(\text{A–B}, \text{bisdinitrogen})\} \quad (3)$$

Here $-\rho_{\text{atom}}(\text{A}, X)$ and $\rho_{\text{BO}}(\text{A–B}, X)$ represent the natural atomic charge of atom A and the bond order between atoms A and B, respectively, for species X. An increase of $\Delta\rho_{\text{atom}}(\text{A})$ or $\Delta\rho_{\text{BO}}(\text{A–B})$ indicates a concentration of electron density in atom A or bond A–B, respectively.

We evaluated the donor–acceptor interaction energy between a lone-pair orbital and an antibonding orbital in the bisdinitrogen complexes, i.e., electron donations from a 4d orbital of Mo to a π^* orbital of N₂ and a σ^* orbital of the P–C bond and those from a lone-pair orbital of amine to a P–C σ^* orbital, by a second-order perturbation theory analysis of the Fock matrix in the natural bond orbital (NBO) basis.^{34b,c} Electron donation to a π orbital of an *N*-phenyl group was estimated as electron donation from a lone pair of an amine to a double bond containing the *ipso*-carbon in the Kekulé structure. In this theory, energy lowering of donor–acceptor interaction is given by eq 4

$$\Delta E^{(2)} = -n_{\text{donor}}^{(0)} \frac{\langle \phi_{\text{donor}}^{(0)} | \hat{F} | \phi_{\text{acceptor}}^{(0)} \rangle^2}{\epsilon_{\text{acceptor}}^{(0)} - \epsilon_{\text{donor}}^{(0)}} \quad (4)$$

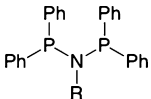
where $\phi_{\text{donor}}^{(0)}$ and $\phi_{\text{acceptor}}^{(0)}$ represent NBOs of the donor and acceptor, $\hat{F}$ represents the Fock operator, and $\epsilon_{\text{donor}}^{(0)}$ and $\epsilon_{\text{acceptor}}^{(0)}$ represent NBO orbital energies of the donor and acceptor.

All electronic structure calculations were performed with the Gaussian 09 package³⁵ on the Fujitsu HX600 system at the Nagoya University Information Technology Center.

RESULTS AND DISCUSSION

Synthesis and Characterization of Some Diphosphinoamine Ligands. Bis(diphenylphosphino)amine ligands (L^R: R = Ph, Xy, *p*-MeOPh, 3,5-*i*Pr₂Ph, *p*-CNPh, *i*Pr, and H) were synthesized easily from chlorodiphenylphosphine and corresponding amines^{29,31} (anilines and primary amines) except for L^H which was synthesized from 1,1,1,3,3,3-hexamethyldisilazane.³⁰ Table 1 provides ³¹P{¹H} NMR spectral data of diphosphinoamine derivative ligands. ³¹P{¹H} NMR chemical shift values of L^{Ph}, L^{Xy}, L^{MeOPh}, L^{CNPh}, and L^{3,5iPrPh} were detected in a lower magnetic field region compared with that of L^H, and that of L^{iPr} was higher than L^{Ph}.³¹ These results indicate that the electron withdrawing aryl groups cause a decrease in the electron density of the phosphorus atoms through the diphosphinoamine nitrogen atom, and the electron donating alkyl groups cause an increase in the electron density of the phosphorus atoms. On the other hand, δ values of L^{Ph}, L^{Xy}, L^{MeOPh}, L^{CNPh}, and L^{3,5iPrPh} are very similar to each other. Therefore, we can conclude that no correlation exists among these groups. This indicates that the aryl substituent groups do not exert an electronic effect on the phosphorus atoms. Similar behavior has been identified in the

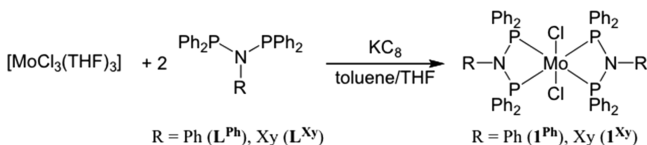
Table 1. $^{31}\text{P}\{^1\text{H}\}$ NMR Data of L^{R} in CDCl_3 (δ/ppm from 85% H_3PO_4)

		
R	δ/ppm	ref
<i>p</i> -MeOPh	70.8	<i>a</i>
3,5- <i>i</i> Pr ₂ Ph	69.5	<i>b</i>
Ph	69.1	<i>c</i>
<i>p</i> -CNPh	68.5	<i>d</i>
Xy	67.2	<i>e</i>
<i>i</i> Pr	48.8	<i>f</i>
H	43.6	<i>g</i>

^aReference 29a. ^bThis work. ^cReference 31a. ^dReference 31b. ^eThis work. ^fReference 20. ^gReference 30.

$^{31}\text{P}\{^1\text{H}\}$ NMR spectral data of *trans*- $[\text{RuCl}_2(\text{L}^{\text{R}})]$ (R = H, Me, Et, *n*Pr, *i*Pr, *n*Bu, and Ph) reported previously.^{29a}

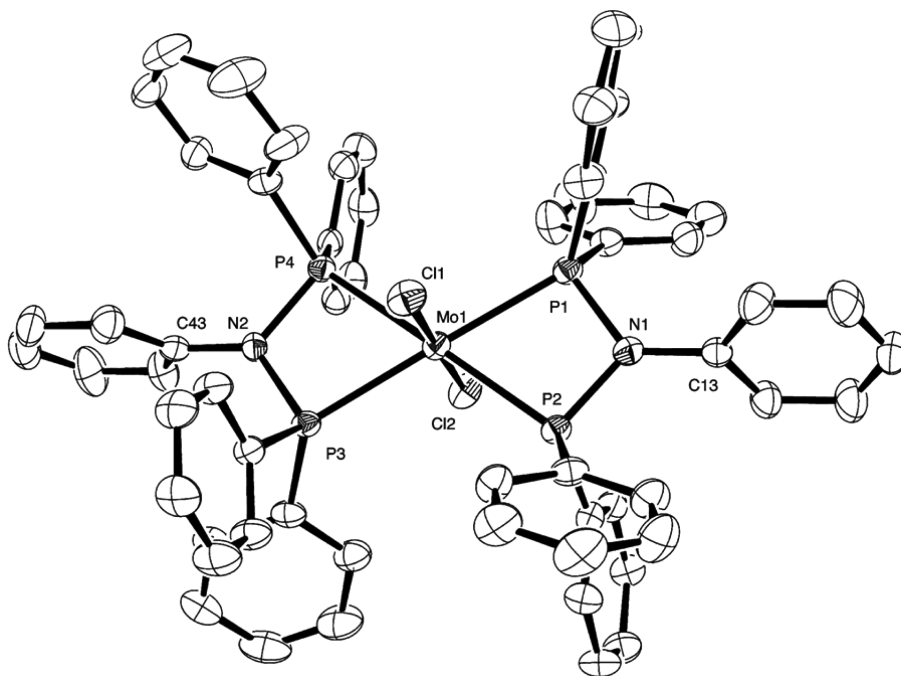
Synthesis and Characterization of *trans*- $[\text{MoCl}_2(\text{L}^{\text{R}})_2]$ Complexes. Treatment of $[\text{MoCl}_3(\text{THF})_3]$ with 2 equiv of diphosphinoamine derivative ligand (L^{Ph} , L^{Xy}) and 1 equiv of KC_8 in THF under an argon atmosphere at room temperature for 12 h gave *trans*- $[\text{MoCl}_2(\text{L}^{\text{R}})_2]$ (R = Ph: L^{Ph} , Xy: L^{Xy}) (Scheme 1). The P–N stretching vibration frequencies $\nu(\text{P}-$

Scheme 1

N) of L^{Ph} and L^{Xy} , as measured by FT-IR spectroscopy, were observed at 862 and 869 cm^{-1} , respectively. These values were

found to shift to a lower energy region relative to those of L^{R} (873 and 872 cm^{-1} for R = Ph and Xy, respectively). These small shift values indicate that L^{R} ligands bind to the metal. The molecular structures of L^{Ph} and L^{Xy} were clarified by X-ray crystallography. ORTEP views of L^{Ph} and L^{Xy} are shown in Figures 1 and 2. Selected interatomic distances and angles for L^{Ph} and L^{Xy} are listed in Table 2. For both L^{Ph} and L^{Xy} , the molybdenum centers are octahedrally coordinated, and two chloride anions are coordinated in with *trans* geometry. Mo–Cl(1) and Mo–Cl(2) bond lengths are 2.3922(8) and 2.4018(8) Å for L^{Ph} and 2.4285(5) and 2.4019(5) Å for L^{Xy} , respectively. The Mo–P bond lengths of L^{Ph} are 2.4832(8) Å for Mo–P(1), 2.5035(7) Å for Mo–P(2), 2.4776(8) Å for Mo–P(3), and 2.4806(7) Å for Mo–P(4), respectively. The Mo–P bond distances of L^{Xy} are 2.4888(6) Å for Mo–P(1), 2.4724(6) Å for Mo–P(2), 2.4660(6) Å for Mo–P(3), and 2.4849 Å for Mo–P(4), respectively. The interatomic distances of Mo⋯N bonds are 3.138(2) and 3.152(2) Å for L^{Ph} and 3.1485(18) and 3.1476(18) Å for L^{Xy} , and the P–N–P angles are 104.70(11)° and 103.10(11)° for L^{Ph} and 103.22(10)° and 103.12(10)° for L^{Xy} , respectively. These findings indicate that the phosphinoamine nitrogen atoms do not bind to the metal ions. In addition, the average P(1)⋯P(4) and P(2)⋯P(3) distances are 4.1733(13) Å and 4.1487(12) Å for L^{Ph} , and 4.1835(8) Å and 4.1079(8) Å for L^{Xy} .

The P–N bond lengths (~1.73 Å) obtained for L^{Ph} and L^{Xy} lie in a usual P–N single bond (1.7–1.8 Å).^{18c,d,36} Although the nitrogen atom of the diphosphinoamine ligand is a tertiary amine, the nitrogen atoms are located within the plane defined by two phosphorus and *ipso* carbon atoms. The nitrogen atom is sp^2 -hybridized. Such hybridization is occasionally found in compounds with a P–N bond.³⁷ Additionally, the aromatic ring attached to the nitrogen atom is largely twisted against the P–N–P plane (ca. 60–90°) as shown also in X-ray crystal structures. The twisting motion that might be attributed to steric interactions with the nitrogen atom has been identified in

**Figure 1.** ORTEP view of *trans*- $[\text{MoCl}_2(\text{L}^{\text{Ph}})_2]$ (L^{Ph}) with 50% thermal ellipsoids. Hydrogen atoms and THF molecules are omitted for clarity.

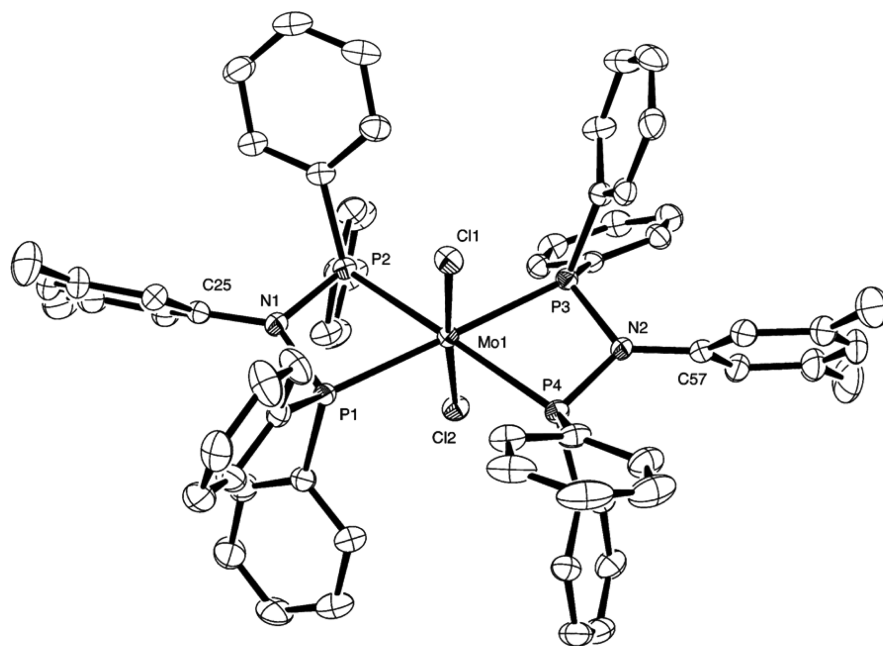


Figure 2. ORTEP view of $\text{trans-[MoCl}_2(\text{L}^{\text{Xy}})_2]$ (1^{Xy}) with 50% thermal ellipsoids. Hydrogen atoms and THF molecules are omitted for clarity.

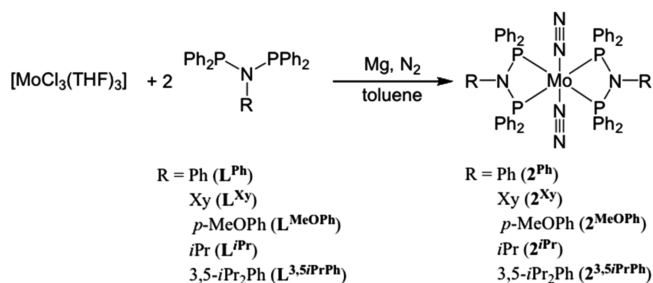
Table 2. Interatomic Distances (Å) and Angles (deg) of 1^{Ph} and 1^{Xy}

complex	1^{Ph}	1^{Xy}
Interatomic Distances (Å)		
Mo(1)–Cl(1)	2.3922(8)	2.4285(5)
Mo(1)–Cl(2)	2.4018(8)	2.4019(5)
Mo(1)–P(1)	2.4832(8)	2.4888(6)
Mo(1)–P(2)	2.5035(7)	2.4724(6)
Mo(1)–P(3)	2.4776(8)	2.4660(6)
Mo(1)–P(4)	2.4806(7)	2.4849(6)
Mo(1)⋯N(1)	3.138(2)	3.1485(18)
Mo(1)⋯N(2)	3.152(2)	3.1476(18)
P(1)⋯P(2)	2.7289(9)	2.7121(8)
P(3)⋯P(4)	2.7142(9)	2.7180(8)
P(1)–N(1)	1.722(2)	1.7294(17)
P(2)–N(1)	1.724(2)	1.7308(19)
P(3)–N(2)	1.735(2)	1.7365(18)
P(4)–N(2)	1.731(2)	1.7335(19)
Bond Angles (deg)		
P(1)–N(1)–P(2)	104.70(11)	103.22(10)
P(3)–N(2)–P(4)	103.10(11)	103.12(10)
P(1)–Mo(1)–P(2)	66.35(2)	66.28(2)
P(3)–Mo(1)–P(4)	66.38(2)	66.59(2)
Dihedral Angles (deg)		
plane[P(1)–N(1)–P(2)]–plane[aryl1]	67.90	64.88
plane[P(3)–N(2)–P(4)]–plane[aryl2]	89.15	77.27

diphosphinoamine ligands without a metal as well as in intramolecular charge-transfer compounds such as *p*-dimethylaminobenzonitrile.^{31b,38,39}

Synthesis and Characterization of Dinitrogen Molybdenum Complexes, $\text{trans-[Mo(N}_2)_2(\text{L}^{\text{R}})_2]$ ($\text{R} = \text{Ph, Xy, iPr, } p\text{-MeO-Ph, 3,5-}i\text{Pr}_2\text{Ph}$). Treatment of $[\text{MoCl}_3(\text{THF})_3]$ with 2 equiv of diphosphinoamine ligand (L^{R}) in the presence of an excess amount of magnesium in toluene under a dinitrogen atmosphere at room temperature for 24 h produces $\text{trans-[Mo(N}_2)_2(\text{L}^{\text{R}})_2]$ ($\text{R} = \text{Ph, 2}^{\text{Ph}}; \text{Xy, 2}^{\text{Xy}}; i\text{Pr, 2}^{\text{iPr}}; p\text{-MeOPh, 2}^{\text{MeOPh}}; 3,5\text{-}i\text{Pr}_2\text{Ph, 2}^{\text{3,5}i\text{Pr}_2\text{Ph}}$) (Scheme 2). Additionally, the ^{15}N -

Scheme 2



enriched dinitrogen molybdenum complexes, $\text{trans-[Mo-(}^{15}\text{N}_2)_2(\text{L}^{\text{R}})_2]$ ($3^{\text{Ph}}, 3^{\text{Xy}}, \text{and } 3^{\text{3,5}i\text{Pr}_2\text{Ph}}$), were prepared by a procedure similar to the procedure used to prepare 2^{R} . In the case of molybdenum complexes 2^{R} with $\text{R} = p\text{-CNPh}$ and H , the corresponding dinitrogen molybdenum complexes were not obtained by synthetic methods similar to the method used in synthesis of 2^{R} . The solubility of dinitrogen molybdenum complexes 2^{R} obtained here is very low, and it is therefore difficult to characterize these complexes in the solution state.

Fortunately, single crystals of 2^{Xy} and $2^{\text{3,5}i\text{Pr}_2\text{Ph}}$ were obtained from THF solution at 238 K. The crystal structures of 2^{Xy} and $2^{\text{3,5}i\text{Pr}_2\text{Ph}}$ were explicitly clarified by X-ray crystallography. ORTEP views of 2^{Xy} and $2^{\text{3,5}i\text{Pr}_2\text{Ph}}$ are shown in Figures 3 and 4. The selected bond lengths and angles are listed in Table 3 for 2^{Xy} and $2^{\text{3,5}i\text{Pr}_2\text{Ph}}$. In addition, a comparison of crystal parameters of several MoN_2 complexes is listed in Table 4. The crystal of 2^{Xy} contains four molybdenum complexes and four disordered THF molecules in the unit cell. The crystal of $2^{\text{3,5}i\text{Pr}_2\text{Ph}}$ contains two slightly different independent molecules of $2^{\text{3,5}i\text{Pr}_2\text{Ph}}$ and four highly disordered THF molecules in the unit cell. In both cases, the molybdenum center is octahedrally six-coordinated with two diphosphinoamine ligands in the equatorial plane and two dinitrogen molecules in *trans* mode in the axial positions. The structures are similar to those of the dichloride molybdenum complexes 1^{Ph} and 1^{Xy} . The aromatic rings of 3,5-dimethylbenzene and 3,5-diisopropylbenzene moieties

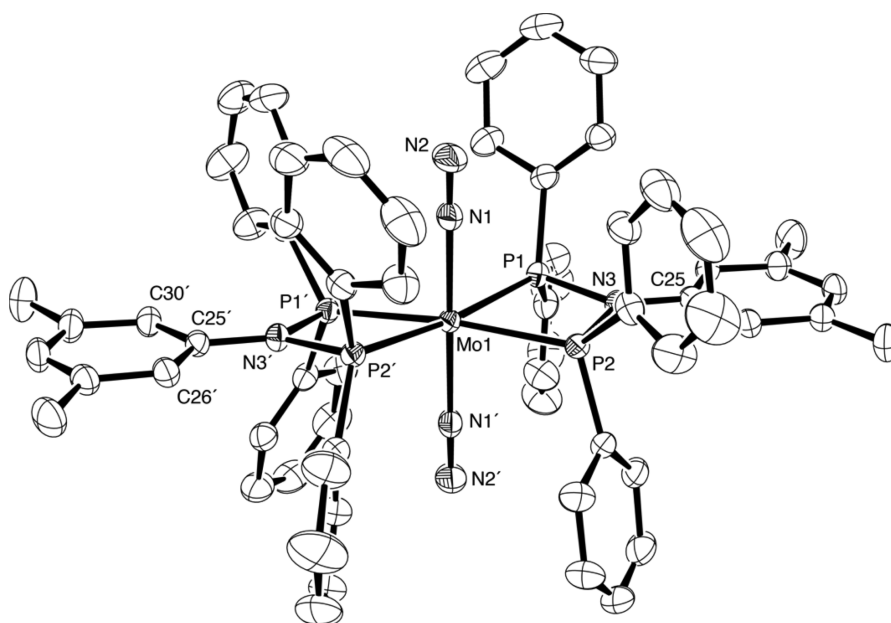


Figure 3. ORTEP view of $\text{trans-}[\text{Mo}(\text{N}_2)_2(\text{L}^{\text{Xy}})_2]$ (2^{Xy}) with 50% thermal ellipsoids. Hydrogen atoms and THF molecules are omitted for clarity.

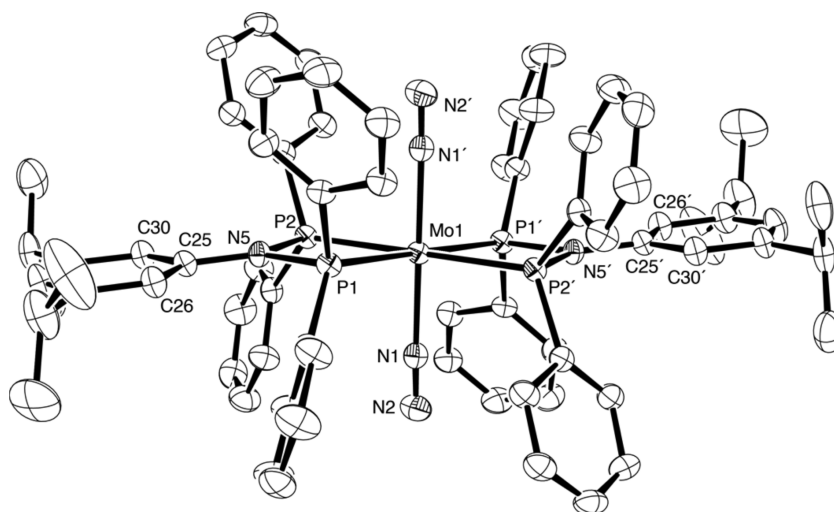


Figure 4. ORTEP view of $\text{trans-}[\text{Mo}(\text{N}_2)_2(\text{L}^{3,5\text{iPrPh}})_2]$ ($2^{3,5\text{iPrPh}}$) with 30% thermal ellipsoids. Hydrogen atoms and THF molecules are omitted for clarity.

attached at the diphosphinoamine nitrogen are only slightly twisted (ca. $3\text{--}6^\circ$) against the P–N–P plane, unlike the twisting observed for 1^{Ph} and 1^{Xy} (ca. $60\text{--}90^\circ$).

The Mo–N₂ bond of 2^{Xy} is $2.0378(18)$ Å for Mo(1)–N(1), and for $2^{3,5\text{iPrPh}}$, the bond lengths are $2.064(4)$ and $2.074(4)$ Å for Mo(1)–N(1) and Mo(2)–N(3), respectively. The Mo–N bond length of the former is shorter than the Mo–N bond lengths of the latter, although these lengths are longer than the Mo–N bond lengths of several previously reported neutral dinitrogen molybdenum complexes with phosphorus ligands: $2.014(5)$ Å for $\text{trans-}[\text{Mo}(\text{N}_2)_2(\text{dppe})_2]$ (dppe = 1,2-bis-(diphenylphosphino)ethane),^{40b} $2.000(5)$ and $1.989(5)$ Å for $\text{trans-}[\text{Mo}(\text{N}_2)_2(\text{PMePh}_2)_4]$,^{40c} and $2.0097(16)$ and $2.0211(15)$ Å for $\text{trans-}[\text{Mo}(\text{N}_2)_2(\text{depf})_2]$ (depf = 1,1'-bis(diethylphosphino)ferrocene).^{40d} The N≡N bond length of the coordinated dinitrogen for 2^{Xy} is $1.110(3)$ Å, which is slightly longer than that of the free dinitrogen molecule (1.095 Å).² In the case of $2^{3,5\text{iPrPh}}$, the N(1)–N(2) ($1.078(6)$ Å) and

N(3)–(4) ($1.058(6)$ Å) bond lengths are shorter than the bond length of the free dinitrogen molecule. Such short N≡N bond lengths of coordinated dinitrogen have been reported previously.⁴¹ These N≡N bond lengths suggest that the coordinated dinitrogen molecule has been hardly activated compared with previous cases ($1.118(8)$ Å for $\text{trans-}[\text{Mo}(\text{N}_2)_2(\text{dppe})_2]$,^{40b} $1.133(7)$ and $1.154(7)$ Å for $\text{trans-}[\text{Mo}(\text{N}_2)_2(\text{PMePh}_2)_4]$,^{40c} and $1.122(2)$ and $1.124(2)$ Å for $\text{trans-}[\text{Mo}(\text{N}_2)_2(\text{depf})_2]$ ^{40d}). The P–N–P angle for 2^{Xy} is $99.32(9)^\circ$ for P(1)–N(3)–P(2), and for $2^{3,5\text{iPrPh}}$ the angles are $99.16(18)^\circ$ for P(1)–N(5)–P(2) and $98.58(17)^\circ$ for P(3)–N(6)–P(4), respectively. These values are $4\text{--}5^\circ$ less than those of 1^{Ph} and 1^{Xy} . These smaller angles are attributed to the twisting of the aryl groups which occurs because the dihedral angles in dichloride molybdenum complexes with a larger P–N–P angle, 1^{Ph} ($104.70(11)$ and $103.10(11)^\circ$) and 1^{Xy} ($103.22(10)$ and $103.12(10)^\circ$), are larger than those of dinitrogen molybdenum complexes with a smaller P–N–P

Table 3. Interatomic Distances (Å) and Angles (deg) of 2^{Xy} and $2^{3,5iPrPh}$

complex	2^{Xy}	$2^{3,5iPrPh}$	
		structure (1)	structure (2)
Interatomic Distances (Å)			
Mo–N ₂	2.0378(18)	2.064(4)	2.074(4)
Mo–P	2.4069(6)	2.4086(11)	2.4026(11)
	2.4130(6)	2.3997(12)	2.4186(13)
P–N	1.7462(16)	1.747(4)	1.736(3)
	1.7432(16)	1.758(4)	1.752(4)
N–N	1.110(3)	1.078(6)	1.058(6)
Mo...N	3.1391(17)	3.132(4)	3.151(4)
P...P	2.6598(7)	2.6516(16)	2.6606(17)
P...P'	4.0027(8) ^a	4.0110(19) ^b	4.0207(18) ^c
Bond Angles (deg)			
P–N–P	99.32(9)	99.16(18)	98.58(17)
P–Mo–P	66.985(17)	66.93(4)	66.99(4)
Dihedral Angles (deg)			
plane[P–N–P]–plane[aryl]	4.667	3.448	6.289

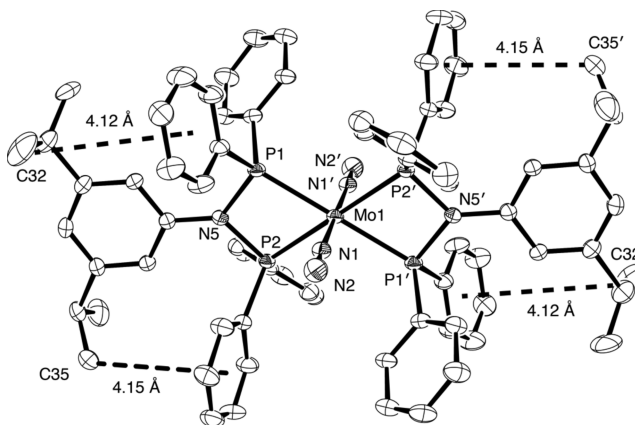
^aThe primed and nonprimed atom are related to each other by the operation $-x + 2, y, -z + 1/2 + 1$. ^bThe primed and nonprimed atom are related to each other by the operation $-x, -y + 2, -z + 1$. ^cThe double primed and nonprimed atom are related to each other by the operation $-x + 1, -y + 2, -z + 2$.

angle, such as 2^{Xy} (99.32(9)°) and $2^{3,5iPrPh}$ (99.16(18) and 98.58(17)°). The aryl groups with a small twisting angle push against the phenyl groups of diphenylphosphines. This results in narrowing of the P–N–P angles. A narrow P–N–P angle causes smaller P...P separations compared with those of 1^{Ph} and 1^{Xy} ; the lengths for 2^{Xy} are 4.0027(8) Å for P(1)...P(1') and 4.0585(8) Å for P(2)...P(2)', and the lengths for $2^{3,5iPrPh}$ are 4.0110(19) Å for P(1)–P(2)', and 4.0207(18) Å for P(3)'–P(4). In addition, the P–Mo–P angle for 2^{Xy} is 66.99(2)° for P(1)–Mo(1)–P(2), and for $2^{3,5iPrPh}$ the angles are 66.93(4)° for P(1)–Mo(1)–P(2) and 66.99(4)° for P(3)–Mo(2)–P(4), respectively. These values are quite small compared with the previous case (79.40(15)° for *trans*-[Mo(N₂)₂(dppe)₂],^{40b} 90.5(2)° for *trans*-[Mo(N₂)₂(PMePh₂)₄],^{40c} and 95.56(2)° and 84.88(2)° for *trans*-[Mo(N₂)₂(depf)₂].^{40d}

The Mo–P bond lengths for 2^{Xy} are 2.4069(6) Å for Mo(1)–P(1) and 2.4130(6) Å for Mo(1)–P(2). The Mo–P bond lengths for $2^{3,5iPrPh}$ are 2.4086(11) Å for Mo(1)–P(1), 2.3997(12) Å for Mo(1)–P(2), 2.4026(11) Å for Mo(2)–P(3), and 2.4186(13) Å for Mo(2)–P(4). These Mo–P bond lengths are shorter than those of 1^{Ph} and 1^{Xy} , although the charges (0) on the central metal of 2^{Xy} and of $2^{3,5iPrPh}$ are less than the +2 charge on the central metal of 1^{Ph} and 1^{Xy} . This result indicates an increase in the covalency of Mo–P bond due to changing in the oxidation states from Mo(+2) to Mo(0). The Mo–P bond lengths observed for 2^{Xy} and $2^{3,5iPrPh}$ lie in a significantly shorter range than those of the *trans*-dinitrogen tetraphosphine molybdenum complexes reported previously

(2.46–2.50 Å).⁴² This shorter Mo–P bond may have been caused by unique property of diphosphinoamine ligand unlike diphosphinomethane ligand.¹⁶

The dihedral angles between the P–N–P plane and N-substituted phenyl ring, as also described above, are 4.7° for 2^{Xy} , and 3.4° and 6.3° for $2^{3,5iPrPh}$. The substituent phenyl rings in these complexes exhibit very little twisting against the P–N–P plane, in contrast with those of 1^R . Although the coplanarity may also be affected by the crystal packing, such examples are quite rare among the metal complexes with N-arylated diphosphinoamine ligands reported previously.^{14a,18g,29c,31b,42} Careful observation of these two crystal structures has revealed an interesting structural feature. As shown in Figure 5, we

**Figure 5.** ORTEP view of $2^{3,5iPrPh}$ with CH– π interactions.

identified a CH– π interaction between xylol methyl groups and the phenyl rings of diphenylphosphine of 2^{Xy} and between the isopropyl methyl groups and the phenyl rings of diphenylphosphine of $2^{3,5iPrPh}$; the distances between methyl carbon atoms (C(31) and C(32) for 2^{Xy} and C(32), C(35), C(68), and C(72) for $2^{3,5iPrPh}$) from the mean plane of phenyl rings are ~4.63 Å for 2^{Xy} and 4.00–4.12 Å for $2^{3,5iPrPh}$, respectively. This CH– π interaction was also identified from the shift of the ring current in ¹H NMR spectra of 2^{Xy} and $2^{3,5iPrPh}$, the methyl protons are shifted to a higher field region relative to those of the diphenylphosphinoamine derivative ligands, and the 3- and 5-methyl protons and 4-protons of 2^{Xy} and the 3- and 5-isopropylmethyl protons and 4-protons of $2^{3,5iPrPh}$ ligands are shifted to an upper field region by 0.01–0.20 ppm relative to those of metal free ligands. The narrow P–N–P angle (~99°) described above may have been induced by the push effect of the methyl groups against the phenyl rings of diphenylphosphine through the CH– π interactions.

In order to clarify the coordination of the dinitrogen molecule to the metal in solution, we synthesized a series of ¹⁵N-enriched dinitrogen molybdenum complexes, 3^R (R = Ph, Xy, 3,5-*iPr*₂Ph). ¹⁵N{¹H} NMR spectra of 3^{Xy} and $3^{3,5iPrPh}$ in

Table 4. Comparison of *trans*-[Mo(N₂)₂(P4)] Complexes

complex	$\nu(\text{N}\equiv\text{N})$ (cm ⁻¹)	N–N (Å)	av Mo–P (Å)	P–Mo–P (deg)
[Mo(N ₂) ₂ (L ^{Xy}) ₂] 2^{Xy}	2011	1.110(3)	2.410(4)	66.99(2)
[Mo(N ₂) ₂ (L ^{3,5iPrPh}) ₂] $2^{3,5iPrPh}$	2014	1.078(6), 1.058(6)	2.407(8)	66.93(4), 66.99(4)
[Mo(N ₂) ₂ (dppe) ₂]	1975	1.118(8)	2.454(10)	79.40(15)
[Mo(N ₂) ₂ (PMePh ₂) ₄]	1922	1.133(7), 1.154(7)	2.496(3)	90.5(2)
[Mo(N ₂) ₂ (depf) ₂]	1907	1.122(2), 1.124(2)	2.493(9)	95.56(2), 84.88(2)

THF solution exhibit two peaks arising from the internal and terminal nitrogens at -46.34 and -45.99 ppm for 3^{Xy} and -46.47 and -46.03 ppm for $3^{3,5\text{IPrPh}}$, respectively (with respect to nitromethane nitrogen as a standard) (Figure S3). These peaks are detected in the lower field region relative to the metal-free dinitrogen molecule (-75.3 ppm) and are in the usual range (-35 to -50 ppm) of the dinitrogen molybdenum complexes reported previously, showing that the dinitrogen molecule binds to molybdenum atoms.⁴³ The chemical shift values and the spin–spin coupling constants of 3^{Xy} and $3^{3,5\text{IPrPh}}$ are similar to those of a “*trans*” isomer of dinitrogen molybdenum complexes (e.g., *trans*-[Mo(N₂)₂(dppe)₂] dppe = 1,2-bis(diphenylphosphino)ethane).^{40b} Therefore, it is suggested that the structures of dinitrogen–molybdenum diphosphinoamine complexes 2^{R} in solution are “*trans*” isomers as shown in the crystal structures.

Solid state FT-IR spectra of 2^{R} show a strong $\nu(\text{N}\equiv\text{N})$ band at 1990 cm^{-1} for 2^{Ph} , 2011 cm^{-1} for 2^{Xy} , 1995 cm^{-1} for 2^{MeOPh} , 2014 cm^{-1} for $2^{3,5\text{IPrPh}}$, and 1975 cm^{-1} for 2^{iPr} . These values are clearly shifted to a lower energy region relative to the corresponding value of the metal-free dinitrogen molecule (2231 cm^{-1}). Additionally, ^{15}N -enriched dinitrogen complexes 3^{R} exhibit an isotope shift of the $\nu(\text{N}\equiv\text{N})$ band at 1923 cm^{-1} for 3^{Ph} ($\Delta 67\text{ cm}^{-1}$), 1934 cm^{-1} for 3^{Xy} ($\Delta 77\text{ cm}^{-1}$), and 1947 cm^{-1} for $3^{3,5\text{IPrPh}}$ ($\Delta 67\text{ cm}^{-1}$). These values appear to be reasonable in considering the isotope effect of the coordinated dinitrogen molecules. These spectral patterns of this observation region are characteristic of the *trans* isomer of dinitrogen molybdenum complexes. The $\nu(\text{N}\equiv\text{N})$ values are listed in Table S1 together with those of previously reported dinitrogen tetraphosphine molybdenum complexes. The $\nu(\text{N}\equiv\text{N})$ values of 2^{R} are also similar to that of the previously reported “*trans*” isomer of tetraphosphine molybdenum complex *trans*-[Mo(N₂)₂(Ph₂PCH₂PPh₂)₂] which has a 4-membered chelate ring (1995 cm^{-1}).^{4c,44}

It is noteworthy that the $\nu(\text{N}\equiv\text{N})$ values of 2^{R} are significantly affected by N-substituent groups of diphosphinoamine ligands; the $\nu(\text{N}\equiv\text{N})$ values decrease according to the following order, $2^{3,5\text{IPrPh}}$ (2014 cm^{-1}) > 2^{Xy} (2011 cm^{-1}) > 2^{MeOPh} (1995 cm^{-1}) > 2^{Ph} (1990 cm^{-1}) > 2^{iPr} (1975 cm^{-1}). These results indicate that the greatest π -back-donation from molybdenum to the dinitrogen molecule is observed for 2^{iPr} . This indicates that 2^{iPr} has the highest electron density on the metal ion. This is quite reasonable in light of the fact that the N-isopropyl group has greater electron donating ability and the N-aryl groups are electron-withdrawing groups. This result may explain the dynamics of the $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shift values for the supporting ligands L^{iPr} . The $^{31}\text{P}\{^1\text{H}\}$ chemical shift value of L^{iPr} is observed in the higher magnetic field region relative to the ^{31}P chemical shift value of L^{Ph} (Table 1). This indicates that the phosphinoamine phosphorus atom of L^{iPr} has the greatest electron density. We can therefore rationalize that the greater electron density on the phosphinoamine phosphorus atom may enhance the extent of electron donation to the molybdenum atom and weaken the extent of π -back-donation from the metal atom to the phosphorus atoms, resulting in enhancement of π -back-donation from molybdenum to the coordinated dinitrogen molecule.

Next, we examine the dynamics of $\nu(\text{N}\equiv\text{N})$ values of 2^{R} with aryl groups. Previously, for the tetraphosphine molybdenum complexes, *trans*-[Mo(N₂)₂(*p*-XC₆H₄CN)(dppe)₂] (*X* = CH₃CO, Cl, H, CH₃, NH₂), and *trans*-[Mo(N₂)₂{(*p*-XC₆H₄)₂PCH₂CH₂P(*p*-XC₆H₄)₂}₂] (*M* = Mo, *X* = CF₃, Cl,

H, CH₃, CH₃O),⁴⁵ Rankin and co-workers reported on a relationship between $\nu(\text{N}\equiv\text{N})$ values and Hammett parameters (σ^+).⁴⁶ They showed that the $\nu(\text{N}\equiv\text{N})$ values (1931 cm^{-1}) of the metal complexes with an electron donating *p*-methoxyphenyl group are smaller than those of metal complexes with a phenyl group (1945 cm^{-1}). However, such a relationship between the $\nu(\text{N}\equiv\text{N})$ values and the electron donating characteristics of L^{R} was not identified. As described in the ^{31}P NMR section above, it is considered that the electron densities on the phosphorus atoms of the phosphinoamine ligands are not affected by the N-substituent aryl groups. For example, the $\nu(\text{N}\equiv\text{N})$ value of 2^{MeOPh} (1995 cm^{-1}) which has the electron donating *p*-methoxyphenyl group is higher than that of 2^{Ph} (1990 cm^{-1}) which has a phenyl group. Similarly, the $\nu(\text{N}\equiv\text{N})$ values of 2^{Xy} (2011 cm^{-1}) and $2^{3,5\text{IPrPh}}$ (2014 cm^{-1}) are higher than that of 2^{Ph} . To clarify these unusual and interesting findings, we perform theoretical study described below.

The $\nu(\text{N}\equiv\text{N})$ value (2011 cm^{-1}) for 2^{Xy} is smaller than that of $2^{3,5\text{IPrPh}}$ (2014 cm^{-1}), although the difference is quite small. Likewise, the average Mo–P bond length of 2^{Xy} ($2.410(4)\text{ \AA}$) is quite similar to that of $2^{3,5\text{IPrPh}}$ ($2.407(8)\text{ \AA}$). In previous reports, it was established that the dinitrogen molybdenum complexes with longer Mo–P bonds tend to show lower $\nu(\text{N}\equiv\text{N})$ values. We identified a correlation between the $\nu(\text{N}\equiv\text{N})$ values and the Mo–P bond lengths, as shown in Figure 6. It was previously found that certain *trans* isomers of

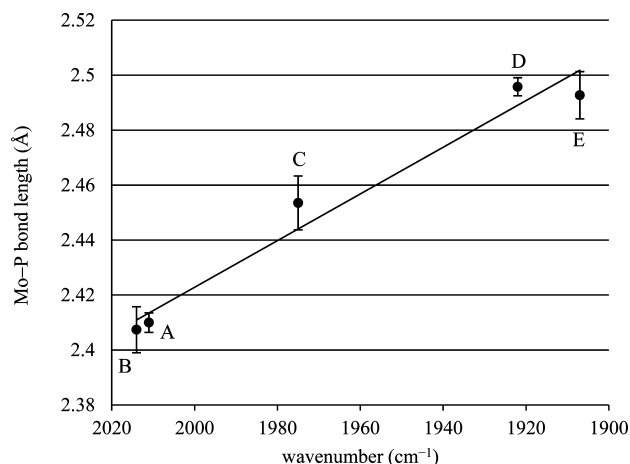


Figure 6. Correlation between the average Mo–P bond lengths (Å) and the $\nu(\text{N}_2)$ values (cm⁻¹) in the *trans*-[Mo(N₂)₂P₄] (P = tertiary phosphine ligand): (A) $2^{3,5\text{IPrPh}}$, (B) 2^{Xy} , (C) *trans*-[Mo(N₂)₂(dppe)₂], (D) *trans*-[Mo(N₂)₂(PMePh₂)₄], (E) *trans*-[Mo(N₂)₂(depf)₂].

tetraphosphine dinitrogen molybdenum complexes which can activate dinitrogen have longer Mo–P bond lengths as follows: *trans*-[Mo(N₂)₂(dppe)₂] ($2.454(10)\text{ \AA}$),^{40b} *trans*-[Mo(N₂)₂(PMePh₂)₄] ($2.496(3)\text{ \AA}$),^{40c} and *trans*-[Mo(N₂)₂(depf)₂] ($2.493(9)\text{ \AA}$).^{40d} A similar relationship is also seen in the substituent effect of diphosphinoamine derivative ligands, which influences Mo–P bond lengths and $\nu(\text{N}\equiv\text{N})$ stretching vibration values of 2^{Xy} and $2^{3,5\text{IPrPh}}$. This effect, however, is very small. In previously reported tetracarbonyl molybdenum complexes with phosphine derivative ligands, such a substituent effect has not been identified in the coordination behavior of the carbonyl molecule which is well-known to exhibit coordination behavior similar to that of the dinitrogen molecule. The $\nu(\text{CO})$ values of the tetracarbonyl

diphenylphosphinoamine complexes $[\text{Mo}(\text{CO})_4\{(\text{PhO})_2\text{PNRP}(\text{OPh})_2\}]$ ($\text{R} = \text{Me}, \text{Ph}$) were essentially the same for the respective substituents.^{29d} In addition, the $\nu(\text{CO})$ stretching vibrations of C-substituted diphenylphosphinomethane complexes $[\text{Mo}(\text{CO})_4\{\text{Ph}_2\text{PC}(\text{R}^1\text{R}^2)\text{PPH}_2\}]$ ($\text{R} = \text{H}, \text{alkyl}, \text{allyl}$) have essentially the same values.⁴⁷ In these cases, the $\nu(\text{CO})$ values of the coordinated carbonyl groups were not affected by the substituent groups. However, in our case, the characteristics of the coordinated dinitrogen molecules are significantly reflected by the $\nu(\text{N}\equiv\text{N})$ values which are influenced by the N-substituent groups; the $\nu(\text{N}\equiv\text{N})$ value ranges between 1975 to 2014 cm^{-1} . This may indicate that equatorial coordination of two diphosphinoamine derivative ligands to the molybdenum ion is favorable for axial coordination of dinitrogen molecules as a result of a through-bond interaction of the $\text{P}-\text{Mo}-\text{N}_2$ moiety. It is therefore quite informative that the N-substituent groups of the diphenylphosphinoamine ligand can indirectly control the electronic properties of metal centers. We have succeeded in controlling the $\nu(\text{N}\equiv\text{N})$ by using the dinitrogen molybdenum complexes with N-substituted diphenylphosphinoamine ligands.

Reactivity of Dinitrogen Diphosphinoamine Molybdenum Complexes. *Efforts To Protonate Dinitrogen Molybdenum Complexes.* To develop dinitrogen reduction catalysts, we first attempted to prepare a hydrazine complex according to a previously reported method using various dinitrogen molybdenum complexes.^{6c,d,48} Complex $2^{3,5\text{IPrPh}}$ was treated with 2 equiv of trifluoromethanesulfonic acid (HOTf) in THF at room temperature for 24 h. The resulting solution was concentrated to dryness, and the precipitate was measured by FT-IR spectroscopy. No peaks assignable to $\nu(\text{N}\equiv\text{N})$ of dinitrogen complex and $\nu(\text{NH})$ of hydrazide complex were observed. In addition, we attempted to generate ammonia by treating complex $2^{3,5\text{IPrPh}}$ with an excess amount of sulfuric acid (H_2SO_4) in THF at room temperature for 24 h.^{6a,b,49} However, formation of ammonia was not detected as measured by using the indophenol method.⁵⁰ In $^31\text{P}\{^1\text{H}\}$ NMR spectra of the resulting residues in benzene- d_6 , there were no peaks corresponding to the diphenylphosphinoamine ligand. This suggests that the supporting ligand of $2^{3,5\text{IPrPh}}$ reacts with acid and decomposes. Burg and Slota have previously reported that the P–N bond of the dimethylaminodimethylphosphine is cleaved by acids such as water and hydrogen chloride.⁵¹ For $2^{3,5\text{IPrPh}}$, it is possible that the P–N bond of the diphenylphosphinoamine ligand has been cleaved by HOTf or H_2SO_4 . Therefore, the coordinated dinitrogen was not reduced to ammonia. Furthermore, this reaction was unsuccessful for all of the other dinitrogen molybdenum complexes with diphosphinoamine ligands. These results indicate that it is difficult for 2^{R} to reduce dinitrogen by protonolysis.

Conversion of Dinitrogen to Silylamine Using Dinitrogen Molybdenum Complexes. Next, we studied the reactivity of the dinitrogen molybdenum complexes 2^{R} toward silylation, because Hidai and co-workers reported catalytic dinitrogen reduction to silylamines using molybdenum- and tungsten-dinitrogen complexes ($\text{TON} = 24.3$).^{4c,52} Treatment of 2^{R} with excess trimethylsilyl chloride and sodium metal in THF under a dinitrogen atmosphere at room temperature for 24 h produced tris(trimethylsilyl)amine and hexamethyldisilazane. Fortunately, the silylation of the coordinated dinitrogen molecules proceeded, although the yields of silylamines were very low. [The turnover numbers

based on the complex detected by GC/MS, $(\text{Me}_3\text{Si})_3\text{N}$, are as follows: 3.95 (2^{Ph}), 0.28 (2^{Xy}), 1.06 (2^{IPr}), 1.03 (2^{MeOPh}), 2.95 ($2^{3,5\text{IPrPh}}$); for $(\text{Me}_3\text{Si})_2\text{NH}$, 0.25 (2^{Ph}), 0.09 (2^{Xy}), 0.35 (2^{IPr}), 0.35 (2^{MeOPh}), 0.48 ($2^{3,5\text{IPrPh}}$). We could not distinguish whether the obtained silylamines were made from dinitrogen or diphosphinoamine ligand. However, any decomposed products from phosphinoamine ligand were not detected in GC/MS chromatogram.] While the silylation of 2^{R} using trimethylsilyl chloride proceeded, the protonation of 2^{R} with acids did not. This may indicate that the trimethylsilyl group (as the species reacting with dinitrogen) is sterically too large to successfully attack the sterically hindered nitrogen atom of the diphosphinoamine ligand. Decomposition of ligands by the reagents was prevented, and then the trimethylsilyl group reacted with dinitrogen preferentially. Since the solubilities of these complexes vary and tend to be quite low, we could not identify a correlation between the reactivities and $\nu(\text{N}\equiv\text{N})$ values of the coordinated dinitrogen molybdenum complexes. We have succeeded in reduction of dinitrogen using molybdenum complexes with diphosphinoamine derivative ligands.

Theoretical Study: Full Optimization of Dinitrogen Molybdenum Complexes by DFT Calculations. The experimental results described above have suggested that the influence of the N-substituent groups of the supporting P–N–P ligands is an important factor in the $\nu(\text{N}\equiv\text{N})$ value. To improve our understanding of the steric and electronic effects of N-substituents, we performed a theoretical study of dinitrogen molybdenum complexes with a particular focus on the dihedral angle between the P–N–P plane and the N-substituted phenyl ring because the values of $\nu(\text{N}\equiv\text{N})$ have been found to be affected by the steric bulk of N-substituted aryl groups. We expect that variations in the dihedral angle may be responsible for this effect. Interestingly, the crystal structures of dichloride–molybdenum complexes indicate large dihedral angles of 67.9° and 89.1° for 1^{Ph} and 64.9° and 77.3° for 1^{Xy} . The dihedral angles of dinitrogen–molybdenum complexes have small dihedral angles of 4.7° for 2^{Xy} and of 3.45° and 6.29° for $2^{3,5\text{IPrPh}}$, respectively. Although this may simply be caused by differences in crystal packing, we focused on these meaningful dihedral angles in our theoretical approach to understand the correlation between the dihedral angle and the behavior of coordinated dinitrogen using geometry optimization and natural population analysis, especially with respect to the differences in electron densities.

The DFT calculations were performed for 2^{Ph} , 2^{Xy} , and $2^{3,5\text{IPrPh}}$ with appropriate dihedral angles (0° and 90°) between the P–N–P plane and the N-substituted phenyl ring plane. Calculations were also carried out for $2(\text{PMe}_2)^{\text{Ph}}$ with dihedral angles of 0° and 90°, where $2(\text{PMe}_2)^{\text{Ph}}$ represents a complex with the diphenylphosphine of 2^{Ph} replaced by dimethylphosphine. For $2(\text{PMe}_2)^{\text{Ph}}$, calculations were also performed for the complex without dinitrogen. For the DFT calculations, the Mo atom was positioned on the origin, the z-axis of d-orbital of Mo atom is placed parallel to the $\text{Mo}-\text{N}(\text{N}_2)$ bonds, and the x-axis is directed toward the diphosphinoamine N atoms. These model complexes were fully optimized using the crystal structures obtained from single crystals of 2^{Xy} and $2^{3,5\text{IPrPh}}$ as their initial bond parameters. The bond parameters for the metal atoms in the structures optimized for 2^{Ph} , 2^{Xy} , $2^{3,5\text{IPrPh}}$, and $2(\text{PMe}_2)^{\text{Ph}}$ with dihedral angles of 0° and 90° are shown in Table S3 together with the estimated $\nu(\text{N}\equiv\text{N})$ stretching vibration values. The whole structures and bond parameters for

the optimized dinitrogen molybdenum complexes are similar to those obtained from the crystal structures within experimental error. However, elongations were identified in the Mo–P bond lengths of the optimized structures.

In the calculations, the substituent effects of N-aryl groups were not observed, although there are significant differences in the Mo–P bond lengths and P–N–P angles between dinitrogen molybdenum complexes with dihedral angles of 0° (coplanar form) and 90° (perpendicular form). The Mo–P bond lengths for the complexes with the coplanar form are shorter than those with the perpendicular form. This indicates that for dinitrogen molybdenum complexes with the perpendicular form, the π -back-donation from the Mo ion to the P atoms is smaller than the π -back-donation of the complexes with the coplanar form. The P–N–P angles (~99°) of the dinitrogen molybdenum complexes with the coplanar form were found to be narrower than the P–N–P angles of the dinitrogen molybdenum complexes with the perpendicular form (~103°). This may be explained by the steric repulsion which occurs between the two phenyl groups of the diphenylphosphine and the N-aryl substituents with the coplanar form. The greater repulsion narrows the P–N–P angle, while the perpendicular form has less repulsion and does not enforce an acute angle. Such behavior is also seen in the crystal structures of **1**^{Ph} (av 103.9°)/**1**^{Xy} (av 103.2°) and **2**^{Xy} (99.32°)/**2**^{3,5iPrPh} (av 98.87°).

In the estimated $\nu(\text{N}\equiv\text{N})$ stretching vibration values, the dinitrogen molybdenum complexes with the perpendicular form (2040 cm⁻¹) have lower frequencies than with the coplanar form (2060 cm⁻¹), although such behavior was found to not be affected by the substituent effect of the N-aryl groups.

To simplify the DFT calculations, we also analyzed dinitrogen molybdenum complexes with diphenylphosphine replaced by dimethylphosphine (**2**(PMe₂)^{Ph}). The entire structure and parameters of the bonds to the metal atoms are essentially identical to those calculated for complexes **2**^{Ph}, **2**^{Xy}, and **2**^{3,5iPrPh} described above (see also Table S3). The most significant change is within 0.01 Å for the Mo–P bonds. The estimated $\nu(\text{N}\equiv\text{N})$ bands also exhibit the same tendency.

Theoretical Study: Natural Population Analysis of the Model Dinitrogen Molybdenum Complexes. In order to examine the natural atomic charges and atom–atom overlap-weighted NAO bond orders of the model dinitrogen molybdenum complexes, we performed a natural population analysis of **2**^{Ph}, **2**^{Xy}, **2**^{3,5iPrPh}, and **2**(PMe₂)^{Ph} (Table S4). The orientations of the N-aryl groups (perpendicular and coplanar forms) exert a significant effect on the natural atomic charges and NAO bond order, but the substituents of the N-aryl groups do not.

The electron density localized on the diphenylphosphine nitrogen flows into the outer nitrogen of the coordinated dinitrogen molecules through the N–P–Mo–N $\equiv$ N bond when the phenyl groups twist around the N–C bond from the coplanar form. The NAO bond orders of N–P–Mo–N $\equiv$ N bonds alternate between an increase and a decrease relative to the coplanar form. The bond order alternates by twisting of the coplanar form to the perpendicular form. For example, in the case of **2**^{Xy}, it decreases for N–C (0.845 → 0.813), increases for N–P (0.630 → 0.634), decreases for Mo–P (0.830 → 0.821), increases for Mo–N (0.841 → 0.856), and decreases for N $\equiv$ N (1.568 → 1.565). These findings suggest that the dinitrogen molecule of the molybdenum dinitrogen complex

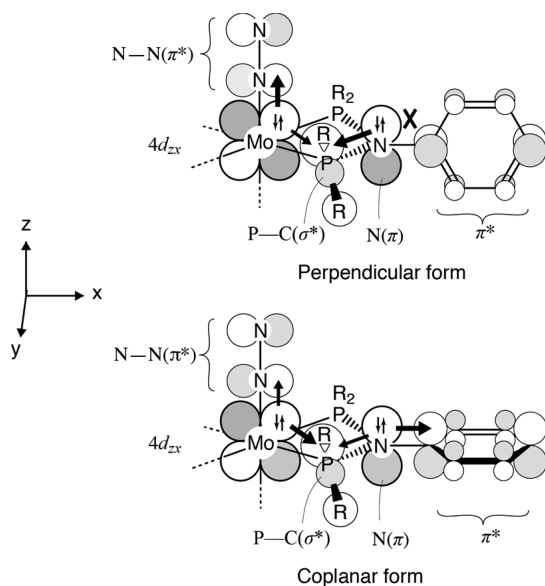
with an N-aryl group in the perpendicular form is negatively charged. This is favorable for attack of external protons.

Theoretical Study: Change in Electronic Structures of the Molybdenum Complex by Coordination of the Dinitrogen Molecule. The calculation of **2**(PMe₂)^{Ph} without dinitrogen molecules was carried out using the four-coordinate diphosphinoamine molybdenum model complex from which dinitrogen molecules were removed **2**(PMe₂)^{Ph}. The calculation of the metal-free dinitrogen molecule was carried out using the structure that was removed from the four-coordinate square-planar molybdenum complex from **2**(PMe₂)^{Ph}. The atomic charges and bond orders of these complexes are listed in Table S5. As shown in Table S5, for both **2**(PMe₂)^{Ph} and **2**(PMe₂)^{Ph} complexes with and without dinitrogen molecules, the total energy is lower with the perpendicular form than with the coplanar form. The atomic charges on molybdenum and dinitrogen were found to increase upon coordination of dinitrogen. The atomic charge on the phosphorus atoms was found to decrease. The order of the N $\equiv$ N bond was found to decrease upon coordination to the metal from 1.804/1.805 to 1.609/1.612 for perpendicular and coplanar forms, respectively. The electron density on the coordinated dinitrogen molecule was found to increase with twisting of the aryl groups from the coplanar form.

The energy levels of the d-orbitals of molybdenum atoms for the complexes with coplanar and perpendicular forms are listed in Table S6. It can be seen that the d-orbitals of the six-coordinate dinitrogen molybdenum complex are doubly occupied in all of the d_{zx} , $d_{x^2-y^2}$, d_{yz} orbitals in this order. The d-orbitals of the four-coordinate molybdenum complex were found to be singly occupied in the $d_{x^2-y^2}$, d_{yz} , d_{zx} , d_{xy} orbitals for α -orbitals and in the $d_{x^2-y^2}$, d_{zx} orbitals for the β -orbitals. The α - and β -orbital energies of the four-coordinate molybdenum complexes are higher for the perpendicular form than those for the coplanar form. This indicates that the d-orbitals of the molybdenum complex with the perpendicular form interact more readily with the π^* -orbitals of dinitrogen molecules and induce π -back-donation more effectively than those with the coplanar form. Indeed, the d_{zx} and d_{yz} orbitals for the molybdenum complexes with vertical and coplanar forms are largely stabilized by dinitrogen coordination compared with the other d-orbitals. The d_{zx} orbital energy is changed between perpendicular and coplanar forms. This behavior has also been identified in the occupation numbers of the d-orbitals of the Mo atom and the p-orbital of the diphenylphosphine N atom. The occupation numbers of both the α - and the β -orbitals are larger in the perpendicular form than the coplanar form, and the occupation numbers of the α - and β - d_{zx} orbitals are especially larger, as shown in Table S7.

As shown in Table S8, the extent of electron donation from the Mo d orbitals to the N₂ π^* orbitals is competitive with the extent of electron donation to the σ^* orbitals of the P–C bonds. This electron donation to the σ^* orbitals of P–C bonds is also competitive with the electron donation from the p-type lone-pair of the diphenylphosphine nitrogen which is in so-called hyperconjugation. The competitive electron donation involving the σ^* orbitals of the P–C bonds is demonstrated in Scheme 3, where the thickness of the arrows shows the magnitude of donation. The significant electron donation originating from the lone-pair of the diphenylphosphine nitrogen inhibits electron donation from the Mo d orbitals to the P–C σ^* orbitals. This inhibition of electron donation (Table S8) is larger in the dinitrogen molybdenum complex

Scheme 3. Comparison of Hyperconjugation Schemes of the Dinitrogen Molybdenum Complex with the Perpendicular Form (Top) and the Coplanar Form (Bottom)^a



^aThe Mo atom was positioned on the origin, the z-axis of *d*-orbital of Mo atom is placed parallel to the Mo–N(N₂) bonds, and the x-axis is directed toward the diphosphinoamine N atoms.

with the perpendicular form relative to that of the N₂ molybdenum complex with the coplanar form. In the dinitrogen molybdenum complex with perpendicular phenyl groups, the occupation numbers of the lone-pair electrons on the diphosphinoamine nitrogen are greater. The extent of electron donation from the lone-pairs to the σ* orbitals of P–C bonds is also greater, and the extent of electron donation from the 4d_{zx} orbital to the σ* orbitals of P–C bonds is less than that of the coplanar form.

The electron densities of the lone-pairs of the diphosphinoamine groups are delocalized to a phenyl group parallel to the P–N–P plane, and the basicity of the diphosphinoamine nitrogen decreases in a manner similar to that of the amino group of aniline. In contrast, the electron density within the dinitrogen molybdenum complex with vertical phenyl groups remains high and is transferred to the σ* orbitals of P–C bonds. Electron donation from the Mo atom to σ* orbitals of P–C bonds is inhibited, and this increases the d-electron donation from Mo to π* orbitals of the N₂ ligands. The interaction between the d_{zx} orbital of Mo and the σ* orbital of P–C bond gives an unusual property due to the small bite angle of the diphosphinoamine ligand. In the larger P–Mo–P angle structure reported previously, however, the phosphorus atoms are located near along the diagonal lines of the regular octahedron. Therefore, it is difficult for the σ* orbital of P–C bond to interact with d_{zx} orbital of Mo ion.

These theoretical results indicate that the nitrogen lone-pair of the diphosphinoamine ligand controls the electron density at the metal center (including phosphorus and dinitrogen). This effect is sometimes seen in molybdenum complexes with diphosphinoamine ligands, and not in the case of metal complexes with carbon-bridged bidentate phosphine ligands such as diphenylphosphinomethane and diphenylphosphinoethane.^{19b,47}

Interpretation of the Difference Between Experimental and Theoretical Results. In the present work we synthesized new dinitrogen molybdenum complexes with diphosphinoamine derivative ligands which form a 4-membered chelate ring and investigated the ability of these complexes. As considered from the $\nu(\text{N}\equiv\text{N})$ stretching vibration values of the dinitrogen molybdenum complexes, the dinitrogen molybdenum complexes with an alkyl group are more effective at decreasing the bond strength of the coordinated dinitrogen molecule than the complexes that have an aryl group. Among the complexes with aryl groups, the $\nu(\text{N}\equiv\text{N})$ values of dinitrogen molybdenum complexes were different from each other. Therefore, in order to explain the effect for the bond strength of dinitrogen, we performed full geometry optimization of the dinitrogen molybdenum complexes with the twisted aryl group ($\sim 90^\circ$) (perpendicular form) and with the nontwisted aryl group ($\sim 0^\circ$) (coplanar form) at the DFT level. Interestingly, the DFT study has suggested that the perpendicular form would be more effective at decreasing the bond strength of dinitrogen molecule than the coplanar form. This behavior has been elucidated as follows: The twisting of aryl groups in the vertical form inhibits π -back-donation from the metal to phosphinoamine. The electron density is pooled on the metal and flows to the coordinated dinitrogen molecule by π -back-donation. This theoretical result can explain the experimental result of the $\nu(\text{N}\equiv\text{N})$ value of dinitrogen molybdenum complexes. **2^{iPr}** has smallest value of $\nu(\text{N}\equiv\text{N})$, because the alkyl substituent group of **2^{iPr}** that does not have π -conjugation system inhibits π -back-donation from the metal to phosphinoamine ligand. Therefore, the order of $\nu(\text{N}\equiv\text{N})$ is **2^{Ph}** > **2^{iPr}**. On the other hand, **2^{Xy}** and **2^{3,5iPrPh}** have the largest value of $\nu(\text{N}\equiv\text{N})$. Interestingly the 3,5-dimethyl groups of the xylyl substituent and the 3,5-diisopropyl groups of the 3,5-diisopropylphenyl substituent interact with the phenyl groups of the diphenylphosphine substituents via a CH– π interaction, as described above in the crystal structure section. Therefore, these complexes have small dihedral angles and small bite angles effect, and the substituent of **2^{3,5iPrPh}** is sterically larger than that of **2^{Xy}**. However, there are no CH– π interactions in **2^{Ph}** and **2^{MeOPh}**; thus, these complexes have large dihedral angles. Also, **2^{MeOPh}** has *p*-methoxy group which has an inductive withdrawing effect. Thus, the order of $\nu(\text{N}\equiv\text{N})$ is **2^{3,5iPrPh}** > **2^{Xy}** > **2^{MeOPh}** > **2^{Ph}**. Consequently, the $\nu(\text{N}\equiv\text{N})$ values decrease according to the following order: **2^{3,5iPrPh}** > **2^{Xy}** > **2^{MeOPh}** > **2^{Ph}** > **2^{iPr}**. The $\nu(\text{N}\equiv\text{N})$ values of **2^R** are significantly affected by N-substituent groups of diphosphinoamine ligands from the viewpoint of both experimental and theoretical study.

CONCLUSION

We have prepared novel molybdenum dinitrogen complexes with P–N–P type diphenylphosphinoamine ligands which form a 4-membered chelate ring as an auxiliary ligand. The $\nu(\text{N}\equiv\text{N})$ values are not clearly reflected in N–N bond distances but indicate that these ligands can control the property of the coordinated dinitrogen through the changes in the structure of metal center according to the properties of the N-substituent groups on the P–N–P ligand. The steric bulkiness of the substituent groups on diphenylphosphinoamine nitrogens contributes to the bond order of the coordinated dinitrogen molecules. This behavior has been elucidated theoretically by DFT calculations. The coplanarity of the N-substituent aryl groups of the P–N–P plane regulates

the flow of electrons from the lone-pair on the nitrogen atom of the P–N–P ligands to the coordinated dinitrogen through the $\pi^*(N_2)-d_{xz},d_{yx}(Mo)-\sigma^*(P-C)$ interaction of the N_2-Mo-P bond. In order to examine the factors controlling the conversion of the molybdenum complexes from dinitrogen to ammonia, we investigated the reduction of dinitrogen by silylation. Reduction was observed, but the yields were quite low. Unfortunately, a correlation between N-substituents and yields of silylamines was not identified because of the low solubility of the molybdenum complexes **2^R**. Here we have investigated the structural effect for dinitrogen coordination by using novel molybdenum complexes with the P–N–P type diphenylphosphinoamine ligands which form a 4-membered chelate ring, and found that the location of phosphorus atoms relative to molybdenum atom (M–P bond lengths and P–M–P bite angles) is very important for controlling the property of coordinated dinitrogen.

■ ASSOCIATED CONTENT

■ Supporting Information

Crystallographic data in CIF format. Additional figures, tables, and details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: masuda.hideki@nitech.ac.jp.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge support for this work provided by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology and the Knowledge Cluster Project. We also thank Yachiyo Taniyama and Hiroko Amano for their helpful support.

■ REFERENCES

- (1) Ertl, G. *The Nobel Prize in Chemistry*; The Royal Swedish Academy of Sciences: Stockholm, 2007.
- (2) Bazhenova, T. A.; Shilov, A. E. *Coord. Chem. Rev.* **1995**, *144*, 69–145.
- (3) Allen, A. D.; Senoff, C. V. *J. Chem. Soc., Chem. Commun.* **1965**, 621–622.
- (4) (a) Allen, A. D.; Harris, R. O.; Loesch, B. R.; Stevens, J. R.; Whiteley, R. N. *Chem. Rev.* **1973**, *73*, 11–20. (b) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589–625. (c) Hidai, M.; Mizobe, Y. *Chem. Rev.* **1995**, *95*, 1115–1133. (d) Hidai, M. *Coord. Chem. Rev.* **1999**, *185–186*, 99–108. (e) Fryzuk, M. D.; Johnson, S. A. *Coord. Chem. Rev.* **2000**, *200–202*, 379–409. (f) Barrière, F. *Coord. Chem. Rev.* **2003**, *236*, 71–89. (g) MacKay, B. A.; Fryzuk, M. D. *Chem. Rev.* **2004**, *104*, 385–401.
- (5) (a) Hidai, M.; Tominari, K.; Uchida, Y.; Misono, A. *J. Chem. Soc. D* **1969**, 814. (b) Hidai, M.; Tominari, K.; Uchida, Y.; Misono, A. *J. Chem. Soc. D* **1969**, 1392. (c) Hidai, M.; Tominari, K.; Uchida, Y. *J. Am. Chem. Soc.* **1972**, *94*, 110–114.
- (6) (a) Chatt, J.; Pearman, A. J.; Richards, R. L. *Nature* **1975**, *253*, 39–40. (b) Chatt, J.; Pearman, A. J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1977**, 1852–1860. (c) Chatt, J.; Dilworth, J. R. *Chem. Commun.* **1975**, 983–984. (d) George, T. M.; Tisdale, C. J. *Am. Chem. Soc.* **1985**, *107*, 5157–5159.
- (7) Fryzuk, M. D.; Love, J. B.; Rettig, S. J.; Young, V. G. *Science* **1997**, *275*, 1445–1447.
- (8) (a) Yoshida, T.; Adachi, T.; Kaminaka, M.; Ueda, T.; Higuchi, T. *J. Am. Chem. Soc.* **1988**, *110*, 4872–4873. (b) Rao, P. V.; Holm, R. H. *Chem. Rev.* **2004**, *104*, 527–559. (c) Lee, S. C.; Holm, R. H. *Chem. Rev.* **2004**, *104*, 1135–1158. (d) Mori, H.; Seino, H.; Hidai, M.; Mizobe, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 5431–5434. (e) Laplaza, C. E.; Cummins, C. C. *Science* **1995**, *268*, 861–863. (f) Smith, J. M.; Sadique, A. R.; Cundari, T. R.; Rodgers, K. R.; Lukat-Rodgers, G.; Lachicotte, R. J.; Flaschenriem, C. J.; Vela, J.; Holland, P. L. *J. Am. Chem. Soc.* **2006**, *128*, 756–769. (g) Bowman, A. C.; Bart, S. C.; Heinemann, F. W.; Meyer, K.; Chirik, P. J. *Inorg. Chem.* **2009**, *48*, 5587–5589.
- (9) (a) Yandulov, D. V.; Schrock, R. R. *Science* **2003**, *301*, 76–78. (b) Schrock, R. R. *Acc. Chem. Res.* **2005**, *38*, 955–962.
- (10) Pool, J. A.; Lobkovsky, E.; Chirik, P. J. *Nature* **2004**, *427*, 527–530.
- (11) (a) Komori, K.; Oshita, H.; Mizobe, Y.; Hidai, M. *J. Am. Chem. Soc.* **1989**, *111*, 1939–1940. (b) Tanaka, H.; Sasada, A.; Kouno, T.; Yuki, M.; Miyake, Y.; Nakanishi, H.; Nishibayashi, Y.; Yoshizawa, K. *J. Am. Chem. Soc.* **2011**, *133*, 3498–3506.
- (12) Arashiba, K.; Miyake, Y.; Nishibayashi, Y. *Nat. Chem.* **2011**, *3*, 120–125.
- (13) (a) Römer, R.; Gradert, C.; Bannwarth, A.; Peters, G.; Näther, C.; Tuczek, F. *Dalton Trans.* **2011**, *40*, 3229–3236. (b) Stephan, G. C.; Näther, C.; Sivasankar, C.; Tuczek, F. *Inorg. Chim. Acta* **2008**, *361*, 1008–1019. (c) Yuki, M.; Midorikawa, T.; Miyake, Y.; Nishibayashi, Y. *Organometallics* **2009**, *28*, 4741–4746. (d) Nishibayashi, Y.; Iwai, S.; Hidai, M. *Science* **1998**, *279*, 540–542. (e) Harvey, B. G.; Arif, A. M.; Ernst, R. D. *Inorg. Chim. Acta* **2010**, *363*, 221–224. (f) Watanabe, D.; Gondo, S.; Seino, H.; Mizobe, Y. *Organometallics* **2007**, *26*, 4909–4920.
- (14) (a) Tuczek, F.; Lehnert, N. *Angew. Chem., Int. Ed.* **1998**, *37*, 2636–2638. (b) Lehnert, N.; Tuczek, F. *Inorg. Chem.* **1999**, *38*, 1659–1670. (c) Lehnert, N.; Tuczek, F. *Inorg. Chem.* **1999**, *38*, 1671–1682. (d) Horn, K. H.; Lehnert, N.; Tuczek, F. *Inorg. Chem.* **2003**, *42*, 1076–1086. (e) Horn, K. H.; Böres, N.; Lehnert, N.; Mersmann, K.; Näther, C.; Peters, G.; Tuczek, F. *Inorg. Chem.* **2005**, *44*, 3016–3030.
- (15) (a) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313–348. (b) van Leeuwen, P. W. M. N.; Kamer, P. C. J.; Reek, J. N. H.; Dierkes, P. *Chem. Rev.* **2000**, *100*, 2741–2769. (c) Freixa, Z.; van Leeuwen, P. W. N. *M. Dalton Trans.* **2003**, 1890–1901.
- (16) Klatt, K.; Näther, C.; Tuczek, F. *Acta Crystallogr.* **2008**, *E64*, m1382.
- (17) (a) Bollmann, A.; Blann, K.; Dixon, J. T.; Hess, F. M.; Killian, E.; Maumela, H.; McGuinness, D. S.; Morgan, D. H.; Neveling, A.; Otto, S.; Overett, M.; Slawin, A. M. Z.; Wasserscheid, P.; Kuhlmann, S. *J. Am. Chem. Soc.* **2004**, *126*, 14712–14713. (b) McGuinness, D. S.; Overett, M.; Tooz, R. P.; Blann, K.; Dixon, J. T.; Slawin, A. M. Z. *Organometallics* **2007**, *26*, 1108–1111. (c) McGuinness, D. S. *Chem. Rev.* **2011**, *111*, 2321–2341.
- (18) (a) Balakrishna, M. S.; Reddy, V. S.; Krishnamurthy, S. S.; Nixon, J. F.; St. Laurent, J. C. T. R. B. *Coord. Chem. Rev.* **1994**, *129*, 1–90. (b) Witt, M.; Roesky, H. W. *Chem. Rev.* **1994**, *94*, 1163–1181. (c) Appleby, T.; Woollins, J. D. *Coord. Chem. Rev.* **2002**, *235*, 121–140. (d) Fei, Z.; Dyson, P. J. *Coord. Chem. Rev.* **2005**, *249*, 2056–2074. (e) Benito-Garagorri, D.; Kirchner, K. *Acc. Chem. Res.* **2008**, *41*, 201–213. (f) Brown, G. M.; Finholt, J. E.; King, R. B.; Lee, T. W. *J. Am. Chem. Soc.* **1981**, *103*, 5249–5250. (g) Tarassoli, A.; Chen, H.; Thompson, M. L.; Allured, V. S.; Haltiwanger, R. C.; Norman, A. D. *Inorg. Chem.* **1986**, *25*, 4152–4157. (h) Brown, G. M.; Finholt, J. E.; King, R. B.; Lee, T. W. *J. Am. Chem. Soc.* **1981**, *103*, 5249–5250. (i) Kubo, K.; Akimoto, T.; Mizuta, T.; Miyoshi, K. *Chem. Lett.* **2008**, *37*, 166–167. (j) Ashby, M. T.; Li, Z. *Inorg. Chem.* **1992**, *31*, 1321–1322. (k) Fei, Z.; Scopelliti, R.; Dyson, P. J. *Inorg. Chem.* **2003**, *42*, 2145–2130. (l) Trinquier, G.; Ashby, M. T. *Inorg. Chem.* **1994**, *33*, 1306–1313. (m) Poetschke, N.; Nieger, M.; Khan, M. A.; Niecke, E.; Ashby, M. T. *Inorg. Chem.* **1997**, *36*, 4087–4093. (n) Priya, S.; Balakrishna, M. S.; Mague, J. T. *J. Organomet. Chem.* **2003**, *679*, 116–124. (o) Fedotova, Y. V.; Kornev, A. N.; Sushev, V. V.; Kursky, Y. A.; Mushtina, T. G.; Makarenko, N. P.; Fukin, G. K.; Abakumov, G. A.; Zakharov, L. N.; Rheingold, A. L. *J. Organomet. Chem.* **2004**, *689*, 3060–3074. (p) Kremer, T.; Hampel, F.; Knoch, F. A.; Bauer, W.;

- Schmidt, A.; Gabold, P.; Schtz, M.; Ellermann, J.; Schleyer, P. V. R. *Organometallics* **1996**, *15*, 4776–4782. (q) Kubo, K.; Nakazawa, H.; Inagaki, H.; Miyoshi, K. *Organometallics* **2002**, *21*, 1942–1948. (r) Blaurock, O. K. S.; Sieler, J.; Hey-Hawkins, E. *Polyhedron* **2001**, *20*, 111–117. (s) Fenske, D.; Maczek, B.; Maczek, K. Z. *Anorg. Allg. Chem.* **1997**, *623*, 1113–1120. (t) Gray, G.; Kraihanzel, C. S. *J. Organomet. Chem.* **1978**, *146*, 23–37. (u) Durap, F.; Biricik, N.; Gümgüm, B.; Özkaz, S.; Ang, W. H.; Fei, Z.; Scopelliti, R. *Polyhedron* **2008**, *27*, 196–202.
- (19) (a) Ahuja, R.; Samuelson, A. G. *J. Organomet. Chem.* **2009**, *694*, 1153–1160. (b) Jiang, T.; Zhang, S.; Jiang, X.; Yang, C.; Niu, B.; Ning, Y. *J. Mol. Catal. A: Chem.* **2008**, *279*, 90–93. (c) Dulai, A.; McMullin, C. L.; Tenza, K.; Wass, D. F. *Organometallics* **2011**, *30*, 935–941.
- (20) Cross, R. J.; Green, T. H.; Keat, R. *J. Chem. Soc., Dalton Trans.* **1976**, 1424–1428.
- (21) (a) Burgess, B. K. *Chem. Rev.* **1990**, *90*, 1377–1406. (b) Smith, B. E.; Durrant, M. C.; Fairhurst, S. A.; Gormal, C. A.; Grönberg, K. L. C.; Henderson, R. A.; Ibrahim, S. K.; Le Gall, T.; Pickett, C. J. *Coord. Chem. Rev.* **1999**, *185–186*, 669–687. (c) Dos Santos, P. C.; Dean, D. R.; Hu, Y.; Ribbe, M. W. *Chem. Rev.* **2004**, *104*, 1159–1173. (d) Einsle, O.; Tezcan, F. A.; Andrade, S. L.; Schmid, B.; Yoshida, M.; Howard, J. B.; Rees, D. C. *Science* **2002**, *297*, 1696–1700. (e) Spatzal, T.; Aksoyoglu, M.; Zhang, L.; Andrade, S. L. A.; Schleicher, E.; Weber, S.; Rees, D. C.; Einsle, O. *Science* **2011**, *334*, 940.
- (22) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, U.K., 1974; Vol. IV, Table 2.2 A.
- (23) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.
- (24) Creagh, D. C.; McAuley, W. J. *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Boston, 1992; Vol. C, Table 4.2.6.8, pp 219–222.
- (25) Creagh, D. C.; Hubbell, J. H. *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Boston, 1992; Vol. C, Table 4.2.4.3, pp 200–206.
- (26) (a) *CrystalStructure 4.0: Crystal Structure Analysis Package*; Rigaku Corporation: Tokyo, 2000–2010; pp 196–8666. (b) Watkin, D. J.; Prout, C. K. C.; Carruthers, J. R.; Betteridge, P. W. *CRYSTALS Issue 10*; Chemical Crystallography Laboratory: Oxford, 1996.
- (27) Stoffelbach, F.; Saurenz, D.; Poli, R. *Eur. J. Inorg. Chem.* **2001**, *2001*, 2699–2701.
- (28) (a) Carver, F. J.; Hunter, C. A.; Livingstone, D. J.; McCabe, J. F.; Seward, E. M. *Chem.—Eur. J.* **2002**, *8*, 2847–2859. (b) Malkov, A. V.; Figlus, M.; Stončius, S.; Kočovský, P. *J. Org. Chem.* **2007**, *72*, 1315–1325.
- (29) (a) Balakrishna, M. S.; Panda, R.; Mague, J. T. *Polyhedron* **2003**, *22*, 587–593. (b) Killian, E.; Blann, K.; Bollmann, A.; Dixon, J. T.; Kuhlmann, S.; Maumela, M. C.; Maumela, H.; Morgan, D. H.; Nongodlwana, P.; Overett, M. J.; Pretorius, M.; Höfener, K.; Wasserscheid, P. *J. Mol. Catal. A: Chem.* **2007**, *270*, 214–218. (c) Balakrishna, M. S.; Prakasha, T. K.; Krishnamurthy, S. S.; Siriwardane, U.; Hosmane, N. S. *J. Organomet. Chem.* **1990**, *390*, 203–216. (d) Biricik, N.; Durap, F.; Kayan, C.; Gümgüm, B. *Heteroat. Chem.* **2007**, *18*, 613–616.
- (30) Nöth, V. H.; Meinel, L. Z. *Anorg. Allg. Chem.* **1967**, *349*, 225–240.
- (31) (a) Balakrishna, M. S.; Panda, R.; Smith, D. C., Jr.; Klamann, A.; Nolan, S. P. *J. Organomet. Chem.* **2000**, *599*, 159–165. (b) Fei, Z.; Scopelliti, R.; Dyson, P. J. *J. Chem. Soc., Dalton Trans.* **2003**, 2772–2779.
- (32) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
- (33) (a) Andrae, D.; Häussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123–141. (b) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. V. R. *J. Comput. Chem.* **1983**, *4*, 294–301. (c) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654–3665. (d) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213–222. (e) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257–2261.
- (34) (a) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735–746. (b) Weinhold, F.; Landis, C. R. *Valency and Bonding: A Natural Bond Orbital Donor-Acceptor Perspective*; Cambridge University Press: Cambridge, U.K., 2005. (c) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899–926.
- (35) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A. Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision A.02*; Gaussian, Inc.: Wallingford, CT, 2009.
- (36) (a) Schmidpeter, A.; Burget, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 580–581. (b) Braunstein, P.; Hasselbring, R.; Tripicchio, A.; Ugozzoli, F. *J. Chem. Soc., Chem. Commun.* **1995**, 37–38.
- (37) (a) Albright, T. A.; Burdett, J. K. *Problems in Molecular Orbital Theory*; Oxford University Press: New York, 1992; pp 103–104. (b) Browning, C. S.; Farrar, D. H.; Frankel, D. C. *Acta Crystallogr.* **1992**, *C48*, 806–811.
- (38) (a) Grabowski, Z. R.; Rotkiewicz, K. *Chem. Rev.* **2003**, *103*, 3899–4031. (b) Druzhinin, S. I.; Dubbaka, S. R.; Knochel, P.; Kovalenko, S. A.; Mayer, P.; Senyushkina, T.; Zachariasen, K. A. *J. Phys. Chem. A* **2008**, *112*, 2449–2761.
- (39) Ganesamoorthy, C.; Balakrishna, M. S.; Mague, J. T.; Tuononen, H. M. *Inorg. Chem.* **2008**, *47*, 7035–7047.
- (40) (a) Uchida, T.; Uchida, Y.; Hidai, M.; Kodama, T. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2883. (b) Uchida, T.; Uchida, Y.; Hidai, M.; Kodama, T. *Acta Crystallogr.* **1975**, *B31*, 1197–1199. (c) Morris, R. H.; Ressler, J. M.; Sawyer, J. F. *Acta Crystallogr.* **1985**, *C41*, 1017–1019. (d) Yuki, M.; Miyake, Y.; Nishibayashi, Y.; Wakiji, I.; Hidai, M. *Organometallics* **2008**, *27*, 3947–3953. (e) Yuki, M.; Miyake, Y.; Nishibayashi, Y. *Organometallics* **2009**, *28*, 5821–5827.
- (41) (a) Morris, R. H.; Ressler, J. M.; Sawyer, J. F.; Shiralian, M. *J. Am. Chem. Soc.* **1984**, *106*, 3683–3684. (b) Mori, H.; Seino, H.; Hidai, M.; Mizobe, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 5431–5434.
- (42) Chen, H.; Tarassoli, A.; Haltiwanger, R. C.; Allured, V. S.; Norman, A. D. *Inorg. Chim. Acta* **1982**, *65*, L69–L70.
- (43) (a) Chatt, J.; Fakley, M. E.; Richards, R. L.; Mason, J.; Stenhouse, I. A. *J. Chem. Res., Miniprint* **1979**, 0876–0889. (b) Dilworth, J. R.; Donovan-Mtunzi, S.; Kan, C. T.; Richards, R. L. *Inorg. Chim. Acta* **1981**, *53*, L161–L162. (c) Donovan-Mtunzi, S.; Richards, R. L.; Mason, J. *J. Chem. Soc., Dalton Trans.* **1984**, 469–474. (d) Donovan-Mtunzi, S.; Richards, R. L.; Mason, J. *J. Chem. Soc., Dalton Trans.* **1984**, 2429–2433. (e) Donovan-Mtunzi, S.; Richards, R. L.; Mason, J. *J. Chem. Soc., Dalton Trans.* **1984**, 2729–2731. (f) Donovan-Mtunzi, S.; MacDonald, C. J.; Richards, R. L.; Hawkes, G. E.; Mason, J. *J. Chem. Soc., Dalton Trans.* **1985**, 2473–2477. (g) Anderson, S. N.; Richards, R. L.; Hughes, D. L. *J. Chem. Soc., Dalton Trans.* **1986**, 245–252.
- (44) Anker, M. W.; Chatt, J.; Leigh, G. J.; Wedd, A. G. *J. Chem. Soc., Dalton Trans.* **1975**, 2639–2645.
- (45) (a) Tatsumi, T.; Hidai, M.; Uchida, Y. *Inorg. Chem.* **1975**, *14*, 2530–2534. (b) Chatt, J.; Leigh, G. J.; Neukomm, H.; Pickett, C. J.; Stanley, D. R. *J. Chem. Soc., Dalton Trans.* **1980**, 121–127. (c) Hussain, W.; Leigh, G. J.; Ali, H. M.; Pickett, C. J.; Rankin, D. A. *J. Chem. Soc., Dalton Trans.* **1984**, 1703–1708.
- (46) Hammett, L. P. *J. Am. Chem. Soc.* **1937**, *59*, 96–103.
- (47) Hogarth, G.; Kilmartin, J. *J. Organomet. Chem.* **2007**, *692*, 5655–5670.

- (48) (a) Chatt, J.; Heath, G. A.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1974**, 2074–2082. (b) Takahashi, T.; Mizobe, Y.; Sato, M.; Uchida, Y.; Hidai, M. *J. Am. Chem. Soc.* **1979**, *101*, 3405–3407. (c) Baumann, J. A.; George, T. A. *J. Am. Chem. Soc.* **1980**, *102*, 6153–6154. (d) Takahashi, T.; Mizobe, Y.; Sato, M.; Uchida, Y.; Hidai, M. *J. Am. Chem. Soc.* **1980**, *102*, 7461–7467. (e) Anderson, S. N.; Fakley, M. E.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1981**, 1973–1980. (f) Hussain, W.; Leigh, G. J.; Pickett, C. J. *J. Chem. Soc., Chem. Commun.* **1982**, 747–748. (g) Bossard, G. E.; George, T. A.; Howell, D. B.; Koczon, L. M.; Lester, R. K. *Inorg. Chem.* **1983**, *22*, 1968–1970.
- (49) (a) Chatt, J.; Pearman, A. J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1977**, 1852–1860. (b) Hidai, M.; Mizobe, Y.; Takahashi, T.; Uchida, Y. *Chem. Lett.* **1978**, 1187–1188. (c) Takahashi, T.; Mizobe, Y.; Sato, M.; Uchida, Y.; Hidai, M. *J. Am. Chem. Soc.* **1979**, *101*, 3405–3407.
- (50) Weatherburn, M. W. *Anal. Chem.* **1967**, *39*, 971–974.
- (51) Burg, A.; Slota, P. J., Jr. *J. Am. Chem. Soc.* **1958**, *80*, 1107–1109.
- (52) (a) Shiina, K. *J. Am. Chem. Soc.* **1972**, *94*, 9266–9267. (b) Komori, K.; Oshita, H.; Mizobe, Y.; Hidai, M. *J. Am. Chem. Soc.* **1989**, *111*, 1939–1940. (c) Tanaka, H.; Sasada, A.; Kouno, T.; Yuki, M.; Miyake, Y.; Nakanishi, H.; Nishibayashi, Y.; Yoshizawa, K. *J. Am. Chem. Soc.* **2011**, *133*, 3498–3506.