Synthesis, Characterization, and Reactivity of Molybdenum Organohydrazido(2-)Complexes with Phosphines as Ancillary Ligands. X-ray Structures of [Mo(NNPh₂)₂Cl₂(PPh₃)] and [Mo(NNMePh)₂Cl₂(PPh₃)₂]^{0.5}CH₂Cl₂

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The complexes $[Mo(NNPh_2)_2Cl_2(PPh_3)]$ (3), $[Mo(NNMePh_2Cl_2(PPh_3)_2]$ (4), $[Mo(NNRPh_2)_2Cl_2(PMePh_2)_2]$ (R = Ph, 5; R = Me, 6), $[Mo(NNRPh)_2Cl_2(PMe_2Ph)_2]$ (R = Ph, 7; R = Me, 8), and $[Mo(NNRPh)_2Cl_2(dppe)]$ (R = Ph, 9; R = Me, 10) have been obtained in good yields by reaction of $[Mo(NHNRPh)(NNRPh)(acac)Cl_2]$ (R = Me, 1; R = Ph, 2) with PMe_{3-n}Ph_n (n = 1-3) or Ph₂PCH₂CH₂PPh₂ in acetonitrile. In refluxing toluene, 4 undergoes dissociation of a PPh₃ ligand to give [Mo(NNMePh)₂Cl₂(PPh₃)] (11). Complexes 3, 4, and 11 react with an excess of acetylacetone in refluxing acetonitrile to give back 1 or 2. Complexes 3-11 have been studied by ¹H, ³¹P NMR, IR, and UV-visible spectroscopy and by electrochemistry. In addition, compounds 3 and 40.5CH₂-Cl₂ have been characterized by X-ray crystal analyses. Complex 3 is monoclinic, space group $P_{2_1/c}$, with a =21.787(5) Å, b = 17.638(1) Å, c = 20.066(14) Å, $\beta = 95.32(1)^{\circ}$, and Z = 8. The structure was solved using 3965 unique observed reflections; the refinements of 735 variables gave final R and R_w values of 0.049 and 0.053, respectively. Compound 40.5CH₂Cl₂ is triclinic, space group P1, with a = 14.384(12) Å, b = 16.599(6)Å, c = 23.919(11) Å, $\alpha = 77.44(4)^{\circ}$, $\beta = 77.51(1)^{\circ}$, $\gamma = 64.39(2)^{\circ}$, and Z = 4. The structure was solved using 5456 unique observed reflections; the refinements of 901 variables converged to R and R_w values of 0.070 and 0.083, respectively. Complex 3 displays a distorted trigonal bipyramidal geometry with the cis-hydrazido ligands in the equatorial plane, while 4 displays a distorted octahedral geometry with cis-hydrazido and trans-phosphine ligands.

Introduction

Transition metal organohydrazido(2-) complexes are of current interest as potential models of intermediates in nitrogen fixation. Indeed, the protonation of dinitrogen complexes to yield ammonia and hydrazine involves the NNH₂ species as an intermediate.^{2,3} The most commonly employed synthetic routes to organohydrazido(2-) complexes involve (i) protonation and alkylation of organodiazenido complexes, (ii) reaction of a metal halide with either unsymmetrically disubstituted hydrazines, e.g. RR'NNH₂, or their trimethylsilyl derivatives, e.g. Me₃SiNHNRR', and (iii) condensation-type reactions of unsymmetrically disubstituted hydrazines with oxometal complexes, notably oxomolybdenum complexes.^{3,4} A lot of complexes containing the *cis*- $[Mo(NNRR')_2]^{2+}$ and cis- $[MoO(NNRR')]^{2+}$ units have now been synthesized, and some of them have been authenticated by X-ray diffraction studies. The cis-[Mo(NNRR')₂]²⁺ unit is present in a number of complexes with ancillary (N,S),⁵ (O,S),⁶ (S,S),⁷⁻¹⁰ (N,N),¹⁰ and (O,O)¹¹ chelated ligands, while the cis-[MoO(NNRR')]²⁺ unit is found in a number of mononuclear

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- (1) (a) Universidad Católica de Valparaíso. (b) Université Pierre et Marie Curie.
- (2) Henderson, R. A.; Leigh, G. J.; Pickett, C. J. Adv. Inorg. Radiochem. 1983. 27. 197.
- (3) McCleverty, J. A. Transition Met. Chem. 1987, 12, 282.
- (4) Mattes, R.; Scholand, H. Angew. Chem., Int. Ed. Engl. 1983, 22, 245.
- (5) Block, E.; Kang, H.; Zubieta, J. Inorg. Chim. Acta 1991, 181, 227.
- (6) Fitzroy, M. D.; Fallon, G. D.; Murray, K. S.; Frederiksen, J. M.;
- Tiekink, R. T. Inorg. Chim. Acta 1990, 169, 79. (7) Dilworth, J. R.; Zubieta, J.; Hyde, J. R. J. Am. Chem. Soc. 1982, 104, 365.
- (8) Dilworth, J. R.; Zubieta, J. A. J. Chem. Soc., Chem. Commun. 1981, 132

complexes containing monodentate thiolate¹² or (O,O),^{6,13,14} (O,S),⁶ (S,S),¹⁵ (N,O),¹⁶ (N,S),⁵ (S,O,S),¹⁷ (S,S,S),¹⁷ (S,N.S),^{17,18} and (S,N,N,S)¹⁹ chelated ligands. Symmetrical^{13,14} and unsymmetrical²⁰ dinuclear molybdenum complexes and organohydrazido-derivatized polyoxomolybdates²¹⁻²³ have also been characterized. The [Mo(NNRR')]⁴⁺ unit has also been described.^{17,24} Although most of the structurally characterized complexes of NNH2²⁻ contain phosphines, there have been comparatively few studies of [organohydrazido(2-)]molybde-

- (9) Chatt, J.; Crichton, B. A. L.; Dilworth, J. R.; Dahlstrom, P.; Gutkoska, R.; Zubieta, J. Transition Met. Chem. 1979, 4, 271.
- (10) Chatt, J.; Crichton, B. A. L.; Dilworth, J. R.; Dahlstrom, P.; Gutkoska, R.; Zubieta, J. Inorg. Chem. 1982, 21, 2383.
- (11) Manzur, C.; Bustos, C.; Carrillo, D.; Robert, F.; Gouzerh, P. To be submitted for publication.
- (12) Burt, R. J.; Dilworth, J. R.; Leigh, G. J.; Zubieta, J. J. Chem. Soc., Dalton Trans. 1982, 2295.
- (13) Bustos, C.; Manzur, C.; Gonzalez, H.; Schrebler, R.; Carrillo, D.; Bois, C.; Jeannin, Y.; Gouzerh, P. Inorg. Chim. Acta 1991, 185, 25. (14) Carrillo, D.; Robert, F.; Gouzerh, P. Inorg. Chim. Acta 1992, 197,
- 209.
- (15) Bishop, M. W.; Chatt, J.; Dilworth, J. R.; Hursthouse, M. B.; Motevalli, M. J. Chem. Soc., Dalton Trans. 1979, 1600.
- (16) Chatt, J.; Crichton, B. A. L.; Dilworth, J. R.; Dahlstrom, P.; Zubieta, J. J. Chem. Soc., Dalton Trans. 1982, 1041.
- (17) Dilworth, J. R.; Hutchinson, J.; Troop, L.; Zubieta, J. Inorg. Chim. Acta 1983, 79, 208.
- (18) Shaikh, S. N.; Zubieta, J. Inorg. Chim. Acta 1986, 115, 19.
- (19) Dahlstrom, P. L.; Dilworth, J. R.; Shulman, P.; Zubieta, J. Inorg. Chem. 1982, 21, 933.
- (20) Shaikh, S. N.; Zubieta, J. Inorg. Chim. Acta 1988, 144, 147.
- (21) Shaikh, S. N.; Zubieta, J. Inorg. Chem. 1986, 25, 4613.

- (22) Shaikh, S. N., Zubieta, J. Inorg. Chem. 1968, 27, 1896.
 (23) Kang, H.; Zubieta, J. J. Chem. Soc., Chem. Comm. 1988, 1192.
 (24) March, F. C.; Mason, R.; Thomas, K. M. J. Organomet. Chem. 1975, 96. C43.

num complexes containing phosphines as ancillary ligands.^{8,10,25-28} This report deals with the synthesis and characterization of [Mo-(NNRPh)₂Cl₂(PPh₃)] (R = Ph, **3**; R = Me, **11**), [Mo(NNMePh)₂-Cl₂(PPh₃)₂] (**4**), [Mo(NNRPh)₂Cl₂(PMePh₂)₂] (R = Ph, **5**; R = Me, **6**), [Mo(NNRPh)₂Cl₂(PMe₂Ph)₂] (R = Ph, **7**; R = Me, **8**) and [Mo(NNRPh)₂Cl₂(dppe)] (R = Ph, **9**; R = Me, **10**), which have been obtained by reaction of [Mo(NHNRPh)(NNRPh)-(acac)Cl₂] (R = Me, **1**; R = Ph, **2**) with the appropriate phosphine in acetonitrile.

Experimental Section

Chemicals. Acetylacetone, 1-methyl-1-phenylhydrazine, 1,1-diphenylhydrazine hydrochloride, triphenylphosphine, methyldiphenylphosphine, dimethylphenylphosphine, 1,2-bis(diphenylphosphino)ethane (dppe), tetrabutylammonium hexafluorophosphate, n-Bu₄NPF₆, and reagent grade solvents were obtained from commercial sources. The complexes [Mo(NHNRPh)(NNRPh)(acac)Cl₂] (R = Me, 1; R = Ph, 2) were prepared as previously described.²⁹

Dichlorobis{diphenylhydrazido(2–)}(triphenylphosphine)molybdenum(VI), [Mo(NNPh₂)₂Cl₂(PPh₃)] (3). PPh₃ (0.17 g, 0.64 mmol) was added to a suspension of complex 2 (0.20 g, 0.32 mmol) in acetonitrile (6 mL). After gentle heating under stirring for 5 min and cooling to room temperature, a green microcrystalline solid was filtered off, washed with diethyl ether, and dried under *vacuo*. The complex was recrystallized from a mixture of *n*-hexane and dichloromethane to yield single crystals suitable for an X-ray structure determination. Yield: 89% (0.22 g). Mp: 184 °C. Anal. Calcd for C₄₂H₃₅Cl₂-MoN₄P: C, 63.6; H, 4.45; N, 7.06. Found: C, 63.2; H, 4.45; N, 7.07. UV-vis [(CH₂Cl₂), λ_{max} , nm (log ϵ)]: 392 (4.11), 376 (sh, 4.10), 296 (sh, 4.26), 234 (4.64). IR (KBr, cm⁻¹): 3080 (w), ν (CH), 1595 (s) ν (NN), 1495 (s) ν (CC). ¹H NMR (CDCl₃): 6.91–7.50 (m, C₆H₅). ³¹P-{¹H</sup> NMR (CDCl₃): 36.98 (s).

Dichlorobis{methylphenylhydrazido(2–)}bis(triphenylphosphine)molybdenum(VI), [Mo(NNMePh)₂Cl₂(PPh₃)₂] (4). The yellow microcystalline solid formed upon gentle heating for 15 min of the mixture of complex 1 (0.20 g, 0.39 mmol) and PPh₃ (0.31 g, 1.18 mmol) in acetonitrile (10 mL) was collected and recrystallized as [Mo-(NNMePh)₂Cl₂(PPh₃)₂]-0.5CH₂Cl₂ (40.5CH₂Cl₂) from dichloromethanediethyl ether. Yield: 60% (0.22 g). Mp: 138 °C dec. Anal. Calcd for C_{50.5}H₄₇Cl₃MoN₄P₂: C, 64.5; H, 4.98; N, 6.01. Found: C, 65.10; H, 5.06; N, 6.00. UV-vis [(CH₂Cl₂), λ_{max} , nm (log ϵ)] 392 (sh, 4.08), 352 (4.19), 236 (4.67). IR (KBr, cm⁻¹): 3080 (w) ν (CH), 2940 (w) ν (CH), 1600 (s) ν (NN), 1490 (s) ν (CC). ¹H NMR (CDCl₃): 3.47 (s, 6H, NCH₃), 5.30 (s, 1H, CH₂Cl₂), 7.02–7.50 (m, 40H, C₆H₅). ³¹P-{¹H} NMR (CDCl₃): 38.02 (s, 1P); -6.19 (s, 1P). Actually, 4 is completely dissociated into 11 and PPh₃ in CDCl₃.

 $Dichlorobis \{ diphenyl hydrazido (2-) \} bis (methyl diphenyl phos$ phine)molybdenum(VI), [Mo(NNPh₂)₂Cl₂(PMePh₂)₂] (5). Complex 2 (1.00 g, 1.58 mmol) and an excess of PMePh₂ (0.96 g, 4.75 mmol) were mixed in acetonitrile (15 mL). After gentle heating for 10 min and cooling to -12 °C, an orange solid deposited within 1 h. This was filtered off, washed with diethyl ether, and recrystallized as 5-CH2- Cl_2 from dichloromethane layered with *n*-hexane at room temperature. Yield: 81% (1.20 g). Mp: 142 °C dec. Anal. Calcd for C₅₀H₄₆Cl₂-MoN₄P₂ (5): C, 64.5; H, 4.98; N, 6.01. Found: C, 63.5; H, 5.24; N, 5.97. UV-vis [(CH₂Cl₂), λ_{max} , nm (log ϵ)]: 388 (4.09), 362 (4.09), 300 (sh, 4.19); 236 (4.61). IR (KBr, cm⁻¹): 3080 (w) ν (CH), 2930 (w) ν (CH), 1600 (s) ν (NN), 1495(s) ν (CC). ¹H NMR [5-CH₂Cl₂ (CDCl₃)]: 2.38 (t, 6H, PCH₃), 5.30 (s, 2H, CH₂Cl₂), 6.96-7.60 (m, 40H, C₆H₅). ³¹P{¹H} NMR (CDCl₃): 25.89 (s), 13.05 (s) and -27.60 (s). Actually, 5 undergoes partial dissociation in CDCl₃ to give [Mo(NNPh₂)₂Cl₂(PMePh₂)] and PMePh₂.

- (25) Crichton, B. A. L.; Dilworth, J. R.; Dahlstrom, P.; Zubieta, J. Transition Met. Chem. 1980, 5, 316.
- (26) Bossard, G. E.; George, T. A.; Lester, R. K.; Tisdale, R. C. Inorg. Chem. 1985, 24, 1129.
- (27) Dilworth, J. R.; Morton, D. L. Transition Met. Chem. 1987, 12, 41.
- (28) George, T. A.; DeBord, J. R. D.; Kwarcinsky, M. E.; Rose, D. J. Abstracts of Papers, 204th National Meeting of the American Chemical Society, Washington, DC; American Chemical Society: Washington, DC, 1992.
- (29) Bustos, C.; Manzur, C.; Carrillo, D.; Robert, F.; Gouzerh, P. Inorg. Chem. 1994, 33, 1427.

Dichlorobis{methylphenylhydrazido(2-)}bis(methyldiphenylphosphine)molybdenum(VI), [Mo(NNMePh)2Cl2(PMePh2)2] (6). Complex 1 (1.00 g, 1.97 mmol) and an excess of PMePh₂ (1.18 g, 5.91 mmol) were mixed in acetonitrile (20 mL). The mixture was stirred and gently heated for 10 min; then the solvent was evaporated under vacuo, diethyl ether was added to the residue,, and the mixture was vigorously stirred overnight. The solid was filtered off and washed with diethyl ether. A yellow microcrystalline solid was obtained from CH2Cl2 layered with n-hexane. This was recrystallized from n-hexanediethyl ether as 6 Et₂O. Yield: 84% (1.33 g). Mp: 146 °C dec. Anal. Calcd for C40H42Cl2MoN4P2 (6): C, 59.5; H, 5.24; N, 6.94. Found: C, 59.8; H, 5.76; N, 6.64. UV-vis $[CH_2Cl_2, \lambda_{max}, nm (log \epsilon)]$: 392 (sh, 4.02), 346 (4.21), 320 (4.21), 238 (4.60). IR (KBr, cm⁻¹): 3070 (w) ν (CH)arom, 2980 (w) ν (CH), 2930 (w) ν (CH), 1600(s) ν (NN), 1495 (s) ν (CC). ¹H NMR [6·Et₂O (CDCl₃)]: 1.21 (t), 2.31 (t), 2.37 (t), 3.02 (s), 3.19 (s), 3.21 (s), 3.48 (q), 6.70-7.60 (m). ${}^{31}P{}^{1}H{}$ NMR (CDCl₃): 14.17 (s), 13.92 (s).

Dichlorobis{diphenylhydrazido(2–)}bis(dimethylphenylphosphine)molybdenum(VI), [Mo(NNPh₂)₂Cl₂(PMe₂Ph)₂] (7). Complex 2 (0.20 g, 0.32 mmol) and PMe₂Ph (0.13 g, 0.95 mmol) were mixed in acetonitrile (10 mL). After gentle heating for 10 min, the solution was cooled to room temperature. A light green solid was obtained after addition of diethyl ether and standing at -12 °C for 2 h. This was filtered off, washed with diethyl ether, and recrystallized from acetonitrile–diethyl ether. Yield: 67% (0.85 g). Mp: 129 °C. Anal. Calcd for C₄₀H₄₂Cl₂MoN₄P₂: C, 59.5; H, 5.24; N, 6.94. Found: C, 59.5; H, 5.32; N, 7.00. UV-vis [(CH₂Cl₂), λ_{max} , nm (log ϵ)]: 392 (sh, 4.02), 344 (sh, 4.11), 302 (4.32), 238 (4.54). IR (KBr, cm⁻¹): 3080 (w) ν -(CH), 2920 (w) ν (CH), 1600 (s) ν (NN), 1495 (s) ν (CC). ¹H NMR (CDCl₃): 1.92 (t, 12H, P(CH₃)₂), 6.60–7.59 (m, 30H, C₆H₅). ³¹P-{¹H</sup> NMR (CDCl₃): 1.24 (s).

Dichlorobis{methylphenylhydrazido(2–)}bis(dimethylphenylphosphine)molybdenum(VI), [Mo(NNMePh)₂Cl₂(PMe₂Ph)₂] (8). A mixture of complex 1 (0.20 g, 0.39 mmol) and PMe₂Ph (0.16 g, 1.18 mmol) in acetonitrile (15 mL) was gently heated for 15 min and then cooled to room temperature. The green precipitate was discarded, and the filtrate was concentrated up to 7 mL under *vacuo*. A yellow solid was obtained after addition of diethyl ether and standing at -12 °C for 3 h. This was recrystallized from diethyl ether—dichloromethane. Yield: 59% (0.24 g). Mp: 162 °C dec. Anal. Calcd for C₃₀H₃₈Cl₂MoN₄P₂: C, 52.7; H, 5.60; C, 8.19. Found: C, 52.8; H, 5.73; N, 8.32. UV-vis [(CH₂Cl₂), λ_{max} , nm (log ϵ)]: 378 (sh, 3.92), 310 (4.42), 238 (4.54). IR (KBr, cm⁻¹): 3080 (w) ν (CH), 2920 (w), ν (CH), 1600 (s) ν (NN), 1495 (s) ν (CC). ¹H NMR (CDCl₃): 1.83 [t, 12 H, P(CH₃)₂], 3.70 (s, 6 H, NCH₃), 5.03 (s, CH₂Cl₂), 6.92-7.50 (m, 20 H, 4 C₆H₅). ³¹P{¹H} NMR (CDCl₃): 1.44 (s).

 $Dichlorobis{diphenylhydrazido(2-)}{bis(1,2-(diphenylphosphi$ no)ethane)}-molybdenum(VI), [Mo(NNPh2)2Cl2(dppe)] (9). A mixture of complex 2 (1.00 g, 1.58 mmol) and dppe (0.69 g, 1.58 mmol) in acetonitrile (25 mL) was gently heated for 10 min. Then, the solvent was evaporated under vacuo, diethyl ether was added to the residue, and the mixture was stirred overnight. The yellow solid was filtered off and dissolved in a mixture of CH₂Cl₂ and *n*-hexane. Under these conditions an oil initially formed, which was separated. Then the solution was allowed to stand for 2 days at -12 °C, to yield large red crystals, which lost CH₂Cl₂ upon standing in air. Stable crystals of 9 were obtained from methanol. Yield: 84% (1.35 g). Mp: 150 °C dec. Anal. Calcd for $C_{50}H_{44}Cl_2MoN_4P_2$ (9): C, 64.6; H, 4.77; N, 6.02. Found: C, 63.5; H, 4.64; N, 5.84. UV-vis [(CH₂Cl₂), λ_{max} , nm (log ϵ)]: 478 (3.25), 370 (4.21), 292 (4.49), 236 (4.71). IR (KBr, cm⁻¹): 3080 (w), v(CH), 2930 (w) v(CH), 1598 (m) v(NN), 1496 (s) v(CC). ¹H NMR (CDCl₃): 2.20-3.50 (m, 4 H, PCH₂CH₂P), 7.11-7.94 (m, 40 H, C_6H_5). ³¹P{¹H} NMR (CDCl₃): 38.35 (d, 1 P), 3.60 (d, 1P), $^{2}J_{P-P}=28.0$ Hz.

Dichlorobis { methylphenylhydrazido(2-) } { bis(1,2-(diphenylphosphino)ethane) } molybdenum(VI), [Mo(NNMePh)₂Cl₂-(dppe)] (10). This complex was synthesized analogously to 9, from 1.00 g (1.97 mmol) of complex 1 and 0.79 g (1.97 mmol) of dppe. The crude complex was recrystallized as 10-CH₂Cl₂ from a mixture of CH₂Cl₂ and *n*-hexane. Yield: 95% (1.67 g). Mp: 145 °C dec. Anal. Calcd for C₄₁H₄₂Cl₄MoN₄P₂: C, 55.3; H, 4.75. Found: C, 54.3; H, 4.73. UV-vis [(CH₂Cl₂), λ_{max} , nm (log ϵ)]: 468 (3.15), 368 (4.09), 292 (4.42), 234 (4.59). IR (KBr, cm⁻¹): 3080 (w), ν (CH), 2940 (w)

Table 1. Summary of Crystallographic Data for Compounds 3 and 4-0.5CH₂Cl₂

	[Mo(NNPh ₂) ₂ Cl ₂ (PPh ₃)]	$[Mo(NNMePh)_2Cl_2(PPh_3)_2] \cdot \\ 0.5CH_2Cl_2$
fw	793.58	974.19
space group	$P2_1/c$	$P\overline{1}$
a, Å	21.787(5)	14.384(12)
<i>b</i> , Å	17.638(1)	16.599(6)
<i>c</i> , Å	20.066(14)	23.919(11)
a, deg	90.0	77.44(4)
β , deg	95.32(1)	77.51(1)
γ , deg	90.0	64.39(2)
$V, Å^3$	7678(7)	4978(12)
Ζ	8	4
<i>T</i> , °C	20	20
λ, Å	0.710 69	0.710 69
μ (Mo K α), cm ⁻¹	5.48	5.18
$\rho_{\rm calc}$, g cm ⁻³	1.37	1.30
R^a	0.049	0.070
R_{w}^{b}	0.053	0.083

 ${}^{a}R = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|. {}^{b}R_{w} = [\sum w(|F_{o}| - |F_{c}|)^{2} / \sum wF_{o}^{2}]^{1/2} (w$ = 1.0).

 ν (CH), 1600 (m) ν (NN), 1495 (sh) ν (CC). ¹H NMR (CDCl₃): 2.15-3.60 (m, 4 H, PCH₂CH₂P), 3.54 (s, NCH₃), 4.14 (s, NCH₃), 5.30 (s, CH₂Cl₂), 7.15-7.99 (m, 30 H, C₆H₅). ³¹P{¹H} NMR (CDCl₃): 42.62 (d) and 9.35 (d), ${}^{2}J_{P-P} = 35.0 \text{ Hz}$; 37.78 (d) and 1.06 (d), ${}^{2}J_{P-P} = 19.8$ Hz.

Dichlorobis{methylphenylhydrazido(2-)}(triphenylphosphine)molybdenum(VI), [Mo(NNMePh)₂Cl₂(PPh₃)] (11). Complex 4 (0.50 g) was refluxed in toluene (10 mL) for 1 h under N_2 . The pale green solid was filtered off, washed with diethyl ether, and recrystallized from toluene. Yield: 92% (0.38 g). Mp: 182 °C. Anal. Calcd for C32H31Cl2MoN4P: C, 57.4; H, 4.67. Found: C, 56.8; H, 4.76. UVvis [(CH₂Cl₂), λ_{max} , nm (log ϵ)]: 390 (sh, 3.81), 354 (3.89), 297 (3.83), 221 (4.38). IR (KBr, cm⁻¹): 3080 (w) v(CH), 2940 (w) v(CH), 1600-(m) v(NN), 1490 (s) v(CC). ¹H NMR (CDCl₃): 3.46 (s, 6 H, NCH₃), 7.02–7.47 (m, 25 H, C₆H₅). ${}^{31}P{}^{1}H{}$ NMR (CDCl₃): 38.05 (s).

Physical Measurements. Melting points were determined by using a Kofler apparatus. Microanalytical data were obtained on a Perkin-Elmer Model 2400 elemental analyzer. IR spectra were recorded on a Perkin-Elmer 599 spectrophotometer as KBr disks. Electronic spectra were recorded in CH2Cl2 solution on a Hewlett Packard 8452A spectrophotometer. ¹H NMR and ³¹P NMR spectra were recorded in CDCl₃ (with TMS and H₃PO₄ as internal and external standards, respectively) on a Bruker AC-200P spectrometer. Cyclic voltammetry (CV) measurements were made with a homemade potentiostat of conventional design, using a standard three-electrode cell with platinum working and auxiliary electrodes and an aqueous saturated calomel electrode (SCE) as the reference. Solution concentrations were 2 mM for the complex under study and 0.1 M n-Bu₄NPF₆ for the supporting electrolyte. All measurements were carried out at room temperature $(15 \pm 2 \ ^{\circ}C)$ under nitrogen in CH₂Cl₂. Under these experimental conditions, the ferrocenium-ferrocene couple was located at +0.50 V.

X-ray Data Collection and Structure Determination of 3 and 40.5CH₂Cl₂. X-ray data were recorded on a Philips PW1100 diffractometer using graphite-monochromated Mo Ka radiation. Crystals were sealed on glass fibers. Lattice parameters and the orientation matrix were obtained from a least-squares fit of the setting angles of 25 automatically centered reflections. Crystal data and data collection parameters are summarized in Table 1. The intensities of two standard reflections were monitored every 1 h; these showed no significant change during data collection. Intensities were corrected for Lorentz and polarization effects. An empirical absorption correction using DIFABS³⁰ was applied. All computations were performed on a Micro VAX II using the CRYSTALS system.³¹ Both structures were solved by direct methods. Hydrogen atoms were not included in the refinements. Anisotropic thermal parameters were refined for all atoms.

Corrections were made for extinction. Final refinements gave R =0.049 and $R_w = 0.053$ for 3 and R = 0.070 and $R_w = 0.083$ for 40.5CH₂-Cl₂. Scattering factors and corrections for anomalous dispersion were taken from ref 32. Atomic positional parameters are listed in Tables 2 and 3. Selected intramolecular bond distances and angles are given in Tables 4 and 5. Views³³ of the molecular structures of 3 and 4 with the atom-labeling scheme are shown in Figures 1 and 2, respectively.

Results and Discussion

Syntheses and Reactivity. In acetonitrile, the complexes $[Mo(NHNRPh)(NNRPh)(acac)Cl_2)] (R = Me, 1; R = Ph, 2)$ react cleanly with phosphines, $PMe_{3-n}Ph_n$ (n = 1-3) to yield neutral diamagnetic mononuclear bis[organohydrazido(2-)]molybdenum(VI) complexes in good yields (see Scheme 1). These species contain either one, e.g. 3 and 11, or two, e.g.complexes 4-8, phosphines. They react similarly with 1,2bis(diphenylphosphino)ethane affording the mononuclear complexes 9 and 10. Complexes 4-10 differ from the cationic complexes $[M(NNMe_2)_2Cl(PR'_3)_2]^+$ obtained by reaction of $[MCl_4(PR'_3)_2]$ (M = Mo, W; PR'_3 = PPh_3, PMePh_2) with Me_3-SiNHNMe₂ in MeCN.^{10,25} The instability of [M(NNMe₂)₂-Cl₂(PR'₃)₂] versus [M(NNMe₂)₂Cl(PR'₃)₂]⁺ could arise from the higher basicity of the Me₂NN²⁻ ligand compared to Ph₂NN²⁻ and PhMeNN²⁻. It is noteworthy that the complexes [Mo- $(NNRPh)_2Cl_2(PR'_3)_2]$ (R = Me, R' = Ph, 4; R = Ph, PR'_3 = PMePh₂, 5) undergo dissociation in CDCl₃ to give complexes [Mo(NNRPh)₂Cl₂(PR'₃)] instead of [Mo(NNRPh)₂Cl(PR'₃)₂]⁺, while complexes $[Mo(NNRPh)_2Cl_2(PR'_3)_2]$ (R = Me, PR'_3 = PMePh₂, **6**; R = Ph, $PR'_3 = PMe_2Ph$, **7**; R = Me, $PR'_3 = PMe_2$ -Ph, 8) are stable toward dissociation. On the other hand, all attempts to synthesize [Mo(NNPh₂)₂Cl₂(PPh₃)₂] were unsuccessful. This indicates that steric effects are operative besides electronic effects. In refluxing acetonitrile, the five-coordinated complexes 3 and 11 and the unstable six-coordinated complex 4 react with acetylacetone to give back complexes 1 and 2. This shows that the interconversion of hydrazido(2-) and hydrazido-(1-) ligands may be forced back and forth by use of suitable ancillary ligands.

X-ray Structures. The asymmetric units of both 3 and 4-0.5CH₂Cl₂ contain two crystallographically independent molybdenum complexes a and b. Moreover that of 4-0.5CH₂Cl₂ contains a molecule of CH₂Cl₂. The geometry about the molybdenum centers in 3 is best described as distorted trigonal bipyramidal with the triphenylphosphine and one chloro ligand occupying the axial positions and the equatorial plane defined by the second chloro group and the α -nitrogen atoms of the two diphenylhydrazido(2-) ligands. The Mo-P and Mo-Cl distances compare well with those of related complexes,^{10,25} and the overall geometry of the hydrazido ligands is similar to that in most organohydrazido(2-) complexes.^{8,10,25} The short Mo-N [1.76(1) Å in (a), 1.75(1) Å in (b)] and N-N distances [1.30(1) and 1.33(1) Å in (a), 1.33(1) and 1.34(1) Å in (b)], thenear linearity of the Mo-N-N grouping [Mo-N-N = 172.9(9)and $176.8(8)^{\circ}$ in (a), 169.3(8) and $172.7(8)^{\circ}$ in (b)], and the near planarity of the Mo-N-N-C2 moieties indicate extensive electronic delocalization throughout the Mo-N-NPh₂ systems. Accordingly, the diphenylhydrazido(2-) ligands may be considered as four-electron donors, and the molybdenum center attains a 18-electron count. The small differences between (a) and (b) probably arise from intra- and intermolecular nonbonding contact interactions rather than from electronic effects.

Molecules a and b in 4-0.5CH₂Cl₂ display similar distorted octahedral geometries. The phosphines occupy two trans-axial

⁽³⁰⁾ Walker, N.; Stuart, D. Acta Crystallogr. 1983, 39A, 158.

Watkin, D. J.; Carruthers, J. R.; Betteridge, P. W. Crystals User Guide; (31)Chemical Crystallography Laboratory, University of Oxford: Oxford, U.K., 1988.

⁽³²⁾ International Tables for X-ray Crystallography; The Kynoch Press: Birmingham, England, 1974; Vol. IV. Pearce, L. J.; Watkin, D. J. CAMERON. Chemical Crystallography

⁽³³⁾ Laboratory, University of Oxford: Oxford, U.K., 1992.

Table 2. Atomic Positional^a and Temperature Factors^b for [Mo(NNPh₂)₂Cl₂(PPh₃)]

atom	x/a	y/b	zlc	$U(eq), Å^2$	atom	x/a	y/b	z/c	$U(eq), Å^2$
Mo(1)	0.67479(5)	0.22964(6)	0.15279(5)	0.0425	Mo(51)	0.82718(5)	0.71446(6)	0.36706(5)	0.0414
Cl(1)	0.7561(2)	0.1559(2)	0.2154(2)	0.0618	Cl(51)	0.7414(2)	0.6435(2)	0.3087(2)	0.0609
Cl(2)	0.6466(2)	0.2618(2)	0.2613(1)	0.0661	Cl(52)	0.8605(2)	0.7301(2)	0.2581(1)	0.0651
P(1)	0.5786(2)	0.3031(2)	0.1137(2)	0.0499	P(51)	0.9266(2)	0.7850(2)	0.4013(1)	0.0461
$\dot{N(1)}$	0.6474(4)	0.1500(6)	0.1059(4)	0.0418	N(51)	0.8480(5)	0.6358(6)	0.4178(4)	0.0457
N(2)	0.6275(5)	0.0874(6)	0.0735(5)	0.0533	N(52)	0.8584(5)	0 5711(6)	0.4514(5)	0.0475
N(11)	0.7243(4)	0.2897(5)	0.1126(4)	0.0435	N(61)	0.7818(4)	0.7825(5)	0.4031(4)	0.0429
N(12)	0.7611(5)	0.3275(6)	0.0774(5)	0.0538	N(62)	0.7454(5)	0.8244(5)	0.4390(5)	0.0502
C(1)	0.6457(4)	0.0709(5)	0.0086(4)	0.0496	C(51)	0.8389(4)	0.5612(5)	0.1370(3)	0.0202
C(2)	0.6447(5)	-0.0038(4)	-0.0136(5)	0.0683	C(52)	0.8070(4)	0.5012(5) 0.4965(5)	0.5321(5)	0.0577
Č(3)	0.6622(5)	-0.0209(5)	-0.0767(5)	0.0873	C(53)	0.7894(4)	0.4871(5)	0.5921(5) 0.5964(5)	0.0795
C(4)	0.6807(5)	0.0367(7)	-0.1178(4)	0.0832	C(54)	0.8037(5)	0.4071(3)	0.5704(5)	0.0790
$\tilde{C}(5)$	0.6817(5)	0.1114(6)	-0.0956(5)	0.0787	C(55)	0.8355(5)	0.5424(7)	0.6787(4)	0.0750
C(6)	0.6642(5)	0.1285(4)	-0.0325(5)	0.0634	C(56)	0.8532(5)	0.6072(0)	0.0207(4)	0.0901
C(7)	0.5932(5)	0.0370(5)	0.0525(5)	0.0557	C(57)	0.0552(5)	0.5126(5)	0.3043(3)	0.0720
C(8)	0.5952(5)	0.0076(7)	0.1706(6)	0.0337	C(58)	0.0011(4) 0.8837(5)	0.5120(5)	0.4174(4)	0.0323
C(0)	0.5862(6)	-0.0432(7)	0.2063(4)	0.0002	C(50)	0.0037(5)	0.5045(3) 0.4509(7)	0.3302(4)	0.0723
C(10)	0.5270(6)	-0.0647(7)	0.1816(6)	0.1002	C(60)	0.9101(0)	0.4053(6)	0.3191(+) 0.3573(6)	0.0952
C(10)	0.5270(0)	-0.0353(7)	0.1010(0) 0.1212(7)	0.1023	C(61)	0.9599(5)	0.4033(0)	0.3375(0)	0.0907
C(12)	0.5009(4)	0.0355(7)	0.1212(7)	0.0933	C(61)	0.9073(+)	0.4134(3)	0.4203(0)	0.0606
C(12)	0.5540(5) 0.7780(4)	0.2067(5)	0.0000(0)	0.0779	C(62)	0.9329(3)	0.4070(3)	0.4373(4)	0.0515
C(13)	0.7760(4)	0.2307(5)	0.01+0(3)	0.0433	C(63)	0.7233(4) 0.7073(5)	0.7931(3) 0.7217(5)	0.5015(3)	0.0313
C(17)	0.8075(4)	0.2270(5) 0.1084(5)	-0.0129(4)	0.0080	C(65)	0.7073(3)	0.7217(5)	0.5000(4)	0.0766
C(15)	0.8237(3) 0.8103(5)	0.190+(3)	-0.0470(0) -0.1063(4)	0.0801	C(03)	0.0939(0)	0.0932(3)	0.3070(0)	0.1052
C(10)	0.8103(3)	0.2390(7)	-0.1003(4)	0.0610	C(00)	0.7051(5)	0.7379(7)	0.0240(4)	0.0920
C(17)	0.7606(3)	0.3093(0) 0.3270(4)	-0.1044(3) -0.0428(5)	0.0098	C(07)	0.7257(5) 0.7201(5)	0.8113(7)	0.0201(4)	0.0815
C(10)	0.7040(4) 0.7017(5)	0.3379(4) 0.3050(5)	-0.0436(3)	0.0599	C(00)	0.7391(3)	0.8398(4)	0.5585(5)	0.0664
C(19)	0.7917(3)	0.3930(3)	0.1040(3)	0.0531	C(09)	0.7214(4)	0.8931(4)	0.4115(4)	0.0459
C(20)	0.8400(3)	0.4224(0) 0.4864(7)	0.0624(3) 0.1120(6)	0.0041	C(70)	0.0082(4)	0.9243(0)	0.4332(4)	0.0000
C(21)	0.8/41(3)	0.4604(7)	0.1120(0) 0.1627(6)	0.0800	C(71)	0.0438(4)	0.9907(6)	0.4042(6)	0.0821
C(22)	0.0470(7)	0.3229(3)	0.1057(0)	0.0661	C(72)	0.0727(5)	1.0258(4)	0.3330(3)	0.0771
C(23)	0.7934(7) 0.7652(4)	0.4933(0)	0.1639(3)	0.1049	C(73)	0.7239(3)	0.9940(5)	0.3319(4)	0.0784
C(24)	0.7033(4)	0.4310(7)	0.1303(3)	0.0848	C(74)	0.7505(4)	0.9283(0)	0.3009(5)	0.0643
C(25)	0.5509(4)	0.2901(5)	0.0247(3)	0.0453	C(75)	0.9470(4)	0.7894(5)	0.4916(3)	0.0380
C(20)	0.5012(4)	0.2572(6)	0.0007(5)	0.0742	C(70)	1.0076(3)	0.7830(5)	0.5193(4)	0.0552
C(27)	0.4878(4)	0.2450(0)	-0.0677(5)	0.0877	C(77)	1.0211(3)	0.7874(5)	0.5883(4)	0.0669
C(28)	0.5301(6)	0.2009(0)	-0.1120(3)	0.0797	C(78)	0.9740(5)	0.7982(5)	0.6295(3)	0.0625
C(29)	0.5858(5)	0.2998(6)	-0.0880(4)	0.0714	C(79)	0.9134(4)	0.8046(5)	0.6017(4)	0.0594
C(30)	0.5992(4)	0.3115(5)	-0.0196(5)	0.0630	C(80)	0.8999(3)	0.8002(5)	0.5328(4)	0.0558
C(31)	0.5110(4)	0.2708(6)	0.1530(4)	0.0562	C(81)	0.9928(4)	0.7408(6)	0.3675(4)	0.0546
C(32)	0.4603(6)	0.3177(5)	0.1580(5)	0.0/1/	C(82)	1.0390(5)	0.7810(5)	0.3396(5)	0.0711
C(33)	0.4084(4)	0.2901(8)	0.1853(5)	0.0863	C(83)	1.0886(4)	0.7427(8)	0.3165(5)	0.0773
C(34)	0.4072(4)	0.2156(8)	0.2077(5)	0.0813	C(84)	1.0921(4)	0.6641(8)	0.3213(5)	0.0838
C(35)	0.45/8(6)	0.1687(5)	0.2027(5)	0.0959	C(85)	1.0459(6)	0.6239(5)	0.3493(6)	0.0843
C(36)	0.509/(5)	0.1963(5)	0.1754(5)	0.0680	C(86)	0.9963(4)	0.6623(6)	0.3723(5)	0.0682
C(37)	0.5809(5)	0.4066(4)	0.1250(5)	0.0552	C(87)	0.9261(5)	0.8852(4)	0.3757(5)	0.0552
C(38)	0.5602(5)	0.4560(6)	0.0737(4)	0.0842	C(88)	0.9271(6)	0.9427(5)	0.4232(3)	0.0719
C(39)	0.5636(6)	0.5339(6)	0.0840(5)	0.0979	C(89)	0.9230(7)	1.0180(5)	0.4030(5)	0.1122
C(40)	0.5876(6)	0.5624(4)	0.1456(6)	0.0866	C(90)	0.9178(7)	1.0359(4)	0.3352(6)	0.1043
C(41)	0.6083(5)	0.5131(6)	0.1968(5)	0.0729	C(91)	0.9168(6)	0.9785(7)	0.2877(4)	0.0888
C(42)	0.6050(5)	0.4352(5)	0.1865(4)	0.0687	C(92)	0.9209(5)	0.9031(6)	0.3080(4)	0.0705

^a Estimated standard deviations in the least significant digits are given in parentheses. ^b $U(eq) = [U(11) \cdot U(22) \cdot U(33)]^{1/3}$.

sites, while the equatorial positions are occupied by two *cis*-hydrazido(2–) ligands and two *cis*-chloro ligands. This arrangement appears to maximize π -bonding interactions. Again, the structural features of the [organohydrazido(2–)]molybdenum moieties fall in the usual ranges.^{8,10,25} However, a small increase in the Mo-N distances, a concomitant decrease in the N–N distances, and a somewhat larger departure from linearity are observed in octahedral [Mo(NNMePh)₂Cl₂(PPh₃)₂] compared to trigonal bipyramidal [Mo(NNPh₂)₂Cl₂(PPh₃)]. Thus, complex 4 achieves a 20-electron count. As a simple molecular orbital scheme might account for the accommodation of the 20 electrons,¹⁰ the unstability of complex 4 toward dissociation probably reflects steric rather than electronic strain.

Spectroscopic Studies. Complexes 3–11 have been studied by IR, UV-visible, ¹H, and ³¹P NMR spectroscopy. As a rule, the IR spectra exhibit a strong and sharp band in the 1600– 1590 cm⁻¹ region, which is tentatively attributed to the ν (NN) stretching mode of the hydrazido(2–) ligands,^{10,18,27,34} and a strong band at *ca.* 1495 cm⁻¹ assigned to a ν (CC) mode of the phenyl groups. The weak band at *ca.* 3255 cm⁻¹ characteristic of the ν (NH) stretching mode of the PhRNNH(1-) ligands²⁹ and the strong band at *ca.* 1570 cm⁻¹ due to the chelated acetylacetonate ligand^{29,35} are notably absent from the IR spectra of complexes **3-11**.

The UV-visible spectra of complexes 3-11 in CH₂Cl₂ solutions show, in general, four absorption bands between 220 and 480 nm. The highest-energy band can be attributed to an internal transition within the phenyl groups, while the other arise from the $[Mo(NNRPh)_2]^{2+}$ chromophore.^{13,14,21}

¹H and ³¹P solution NMR studies of complexes 3-11 have been undertaken to obtain information about their stereochemistry and stability. From the solid-state studies of complexes 3 and $40.5CH_2Cl_2$, it was anticipated that complexes 3 and 11 should possess distorted trigonal bipyramidal geometry in solution, while complexes 4-8 should display distorted octa-

⁽³⁴⁾ Nicholson, T.; Zubieta, J. J. Chem. Soc., Chem. Commun. 1985, 367.

⁽³⁵⁾ Soptrajanov, B.; Nikolovski, A.; Petrov, I. Spectrochim. Acta 1968, 24A, 1617.

Table 3. Atomic Positional^a and Temperature Factors^b for [Mo(NNMePh)₂Cl₂(PPh₃)₂]^{•0.5CH₂Cl₂}

$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$			L		• •	/ ·				
Mer(1) 0.5101(1) 0.41442(2) 0.28682(6) 0.0377 Pf22 0.0689(4) -0.0132(3) 0.0300(2) 0.04472 C1(1) 0.1507(3) 0.5663(3) 0.2438(2) 0.0503 N(52) 0.1637(1) 0.1637(5) 0.04448 P11 0.1687(3) 0.4448(3) 0.3778(2) 0.04423 N(62) 0.0571(1) 0.1533(5) 0.04448 N(1) 0.3741(9) 0.34443(3) 0.3778(2) 0.04423 N(62) 0.0571(1) 0.1533(5) 0.0443 N(2) 0.4493(1) 0.32546(6) 0.0556 C(53) 0.0791(1) -0.1221(9) 0.1415(5) 0.0773 N(1) 0.356(1) 0.445(1) 0.369(0) 0.0560 C(551) -0.058(8) -0.0424(7) 0.1336(6) 0.0775 C(2) 0.448(1) 0.369(1) 0.4491(2) 0.455(1) C(51) -0.059(8) -0.0614(7) 0.1326(6) 0.0569 C(3) 0.566(1) 0.442(2) 0.455(1) C(51) 0.269(1) 0.0521(1) 0.0571(1) <t< th=""><th>atom</th><th>xla</th><th>y/b</th><th>zlc</th><th>$U(eq), Å^2$</th><th>atom</th><th>x/a</th><th>y/b</th><th>zlc</th><th>$U(eq), \dot{A}^2$</th></t<>	atom	xla	y/b	zlc	$U(eq), Å^2$	atom	x/a	y/b	zlc	$U(eq), \dot{A}^2$
$ \begin{array}{c} C(1) \\ 0.2142(3) \\ 0.197(3) \\ 0.563(3) \\ 0.248(4) \\ 0.073(3) \\ 0.563(3) \\ 0.248(4) \\ 0.073(2) \\ 0.063(3) \\ 0.0448(4) \\ 0.0378(2) \\ 0.0442 \\ 0.017(1) \\ 0.063(3) \\ 0.0442(3) \\ 0.01742(3) \\ 0.0187(2) \\ 0.0442(3) \\ 0.01742(3) \\ 0.0187(2) \\ 0.0187(3) \\ 0.$	Mo(1)	0.3101(1)	0.41442(9)	0.28882(6)	0.0377	P(52)	0.0689(4)	-0.0132(3)	0.3050(2)	0.0472
$ \begin{array}{c} C_{12} 0 & 1.907(3) & 0.563(3) & 0.248(2) & 0.0503 & N(52) & 0.163(1) & -0.153(8) & 0.1623(6) & 0.04+48 \\ P(1) & 0.1687(3) & 0.4448(3) & 0.375(2) & 0.04+23 & N(62) & 0.067(1) & 0.1833(9) & 0.1789(6) & 0.04+9 \\ N(1) & 0.3743(9) & 0.4641(8) & 0.3144(5) & 0.0350 & C(51) & 0.067(1) & 0.1833(9) & 0.1789(6) & 0.0544 \\ N(2) & 0.412(1) & 0.1986(9) & 0.3256(6) & 0.0512 & C(52) & 0.088(1) & -0.2107(7) & 0.1063(6) & 0.0524 \\ N(1) & 0.374(1) & 0.2186(9) & 0.3256(6) & 0.0512 & C(53) & -0.088(8) & -0.4922(9) & 0.1393(6) & 0.0554 \\ N(1) & 0.374(1) & 0.2186(9) & 0.3587(7) & 0.0746 & C(55) & -0.088(8) & -0.4922(9) & 0.1303(6) & 0.0755 \\ C(2) & 0.496(1) & 0.399(9) & 0.3887(7) & 0.0741 & C(56) & -0.088(8) & -0.4922(9) & 0.1403(6) & 0.0755 \\ C(3) & 0.560(1) & 0.43(2) & 0.4477(1) & 0.1194 & C(57) & -0.098(1) & -0.4614(7) & 0.1326(6) & 0.0755 \\ C(4) & 0.666(1) & 0.412(2) & 0.4577(6) & 0.1192 & C(58) & -0.098(1) & 0.1664(7) & 0.1326(6) & 0.0466 \\ C(5) & 0.590(1) & 0.498(2) & 0.4264(8) & 0.0986 & C(59) & -0.018(1) & 0.1647(8) & 0.0571 \\ C(6) & 0.520(1) & 0.353(1) & 0.448(1) & 0.0873 & C(60) & -0.018(1) & 0.1647(7) & 0.1075(6) & 0.0617 \\ C(7) & 0.384(2) & 0.614(1) & 0.2953(9) & 0.0638 & C(61) & -0.161(1) & 0.292(1) & 0.071(6) & 0.0763 \\ C(7) & 0.384(2) & 0.648(6) & 0.1625(6) & 0.0773 & C(63) & -0.077(1) & 0.3122(8) & 0.0764 \\ C(10) & 0.545(1) & 0.017(7) & 0.456(6) & 0.0792 & C(53) & 0.0395(9) & 0.1013(6) & 0.0876(7) & 0.991(1) \\ C(13) & 0.645(9) & 0.144(1) & 0.3374(9) & 0.0579 & C(65) & 0.398(9) & 0.1013(6) & 0.0876(7) & 0.991(0) \\ C(14) & 0.655(9) & 0.0428(6) & 0.0779 & C(67) & 0.265(1) & 0.0134(1) & 0.2172(6) & 0.0754 \\ C(10) & 0.545(9) & 0.144(1) & 0.3274(6) & 0.0792 & C(65) & 0.398(9) & 0.1013(6) & 0.087(5) & 0.0498 \\ C(13) & 0.045(1) & 0.0324(9) & 0.0526(6) & 0.0773 & C(65) & 0.398(9) & 0.1013(6) & 0.085(7) & 0.0498 \\ C(14) & 0.255(9) & 0.0428(6) & 0.0779 & C(67) & 0.326(9) & 0.1034(7) & 0.0185(7) & 0.0486(7) \\ C(15) & 0.1374(7) & 0.4374(6) & 0.0472 & C(73) & 0.336(9) & 0.0134(1) & 0.0157(6) & 0.0574 \\ C(14) & 0.057(1) & 0$	Cl(1)	0.2142(3)	0.3640(3)	0.2360(2)	0.0545	N(51)	0.1602(9)	-0.0837(8)	0.1807(5)	0.0358
P11 0.1687(3) 0.4442(3) 0.3778(2) 0.0442 N(61) 0.117(1) 0.0984(9) 0.1837(9) 0.1837(9) 0.1837(9) 0.1837(9) 0.1837(9) 0.1343(5) 0.04462 N(1) 0.37743(9) 0.4681(8) 0.3144(5) 0.0390 C551 0.0793(9) -0.1422(9) 0.1343(5) 0.04460 N(1) 0.393(1) 0.4141(8) 0.04462 C531 -0.0797(1) -0.1422(9) 0.1030(6) 0.0755 C(1) 0.439(1) 0.3947(9) 0.3047(7) 0.0759 0.01759 0.01759 C(2) 0.496(1) 0.3994(9) 0.3937(7) 0.0741 C561 -0.0492(9) 0.1637(8) 0.0555 C(3) 0.566(1) 0.433(1) 0.4117(1) 0.104 C579 -0.0493(1) 0.16647(7) 0.10765(0) 0.0417 C(5) 0.599(1) 0.4982(2) 0.4244(8) 0.9966 (C59) -0.018(1) 0.1564(7) 0.10765(0) 0.0417 C(6) 0.525(1) 0.1563(7) 0.0181(6) 0.0172	C1(2)	0.1907(3)	0.5663(3)	0.2438(2)	0.0503	N(52)	0.163(1)	-0.1538(9)	0.1623(6)	0.0448
P(2) 0.4449(3) 0.9342(3) 0.1952(2) 0.04423 N(22) 0.067(1) 0.1835(9) 0.1789(6) 0.01449 N(1) 0.5174(3) 0.4481(8) 0.3124(5) 0.0366 0.0571(1) 0.1624(2) 0.1315(5) 0.0366(5) 0.0739(1) 0.1624(5) 0.0355 N(1) 0.217(1) 0.2188(8) 0.312(1) 0.3888(8) 0.312(1) 0.0388(8) 0.01755 C(2) 0.496(1) 0.339(1) 0.348(7) 0.0741 0.153(6) 0.0575 C(3) 0.590(1) 0.343(1) 0.4117(1) 0.1194(1) C(58) -0.098(1) 0.164(6) 0.044(6) C(4) 0.666(1) 0.412(2) 0.4547(6) 0.1192 C(58) -0.098(1) 0.164(1) 0.032(1) 0.0371(6) 0.0492 0.0447(8) 0.0087(8) 0.0423 0.014(1) 0.032(1) 0.0771(6) 0.112 0.4571(7) 0.436(1) 0.0271(1) 0.0124(1) 0.0271(1) 0.0124(1) 0.0178(1) 0.0178(1) 0.0174(1) 0.0127(1) 0.014(1)	P(1)	0.1687(3)	0.4448(3)	0.3778(2)	0.0442	N(61)	0.117(1)	0.0984(9)	0.1867(5)	0.0462
$ \begin{array}{c} N(1) & 0.3743(9) & 0.4681(8) & 0.3134(5) & 0.0390 & C(31) & 0.0793(9) & -0.142(9) & 0.1434(3) & 0.0546 \\ N(11) & 0.372(1) & 0.2988(8) & 0.3216(5) & 0.0356 & C(33) & 0.098(1) & -0.19(1) & 0.0766(5) & 0.0735 \\ N(12) & 0.385(1) & 0.2410(9) & 0.3417(6) & 0.0462 & C(33) & -0.098(1) & -0.118(1) & 0.0776(5) & 0.0735 \\ C(1) & 0.480(1) & 0.453(1) & 0.36317(7) & 0.0462 & C(36) & -0.098(1) & -0.118(1) & 0.0776(5) & 0.0535 \\ C(3) & 0.590(1) & 0.453(1) & 0.34317(7) & 0.0442 & C(36) & -0.098(1) & -0.240(1) & 0.1326(5) & 0.0551 \\ C(4) & 0.690(1) & 0.412(2) & 0.4537(6) & 0.1192 & C(38) & -0.098(1) & -0.240(1) & 0.1467(8) & 0.0551 \\ C(5) & 0.590(1) & 0.432(2) & 0.4537(6) & 0.1192 & C(38) & -0.098(1) & 0.240(1) & 0.0776(6) & 0.0467(7) \\ C(5) & 0.526(1) & 0.3350(9) & 0.3831(8) & 0.0881 & C(60) & -0.048(1) & 0.223(1) & 0.0778(6) & 0.0981 \\ C(7) & 0.334(2) & 0.616(6) & 0.0733 & C(63) & -0.078(1) & 0.0278(6) & 0.0981 \\ C(8) & 0.4856(8) & 0.1636(7) & 0.3396(5) & 0.0423 & C(62) & -0.153(1) & 0.3477(8) & 0.1087(6) & 0.0776 \\ C(10) & 0.581(1) & 0.0371(7) & 0.4361(5) & 0.0771 & C(64) & 0.0851(1) & 0.242(8) & 0.078(6) & 0.0752 \\ C(11) & 0.6515(9) & 0.0660(9) & 0.425(6) & 0.0679 & C(66) & 0.389(5) & 0.1013(6) & 0.0587(5) & 0.0498 \\ C(12) & 0.6545(9) & 0.144(1) & 0.3371(6) & 0.0773 & C(63) & 0.226(1) & 0.0273(1) & 0.0321(8) & 0.0734 \\ C(13) & 0.557(1) & 0.1274(7) & 0.3374(9) & 0.0579 & C(68) & 0.228(1) & 0.272(8) & 0.0353(7) & 0.0408 \\ C(13) & 0.6547(9) & 0.144(1) & 0.3374(9) & 0.0579 & C(68) & 0.238(1) & 0.229(8) & 0.0353(7) & 0.0408 \\ C(13) & 0.254(1) & 0.172(6) & 0.0543 & C(77) & 0.335(9) & -0.0118(7) & 0.0486(5) & 0.0754 \\ C(14) & 0.0278(1) & 0.0774 & C(73) & 0.6355(9) & -0.0118(7) & 0.061(4) & 0.0484 \\ C(14) & 0.322(1) & 0.172(7) & 0.458(5) & 0.0779 & C(73) & 0.635(9) & -0.0118(7) & 0.051(5) & 0.0749 \\ C(22) & 0.175(9) & 0.459(6) & 0.0772 & C(73) & 0.635(9) & -0.014(9) & 0.0147(6) & 0.0753 \\ C(24) & 0.173(9) & 0.673(8) & 0.477(6) & 0.0594 & C(77) & 0.3353(9) & -0.0049(9) & 0.0134(6) & 0.0757 \\ C(25) & 0.176(9) & 0.529(1) & 0.57$	P(2)	0.4409(3)	0.3942(3)	0.1955(2)	0.0423	N(62)	0.067(1)	0.1853(9)	0.1789(6)	0.0449
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	N(1)	0.3743(9)	0.4681(8)	0.3134(5)	0.0390	C(51)	0.0793(9)	-0.1422(9)	0.1343(5)	0.0460
$ \begin{array}{c} N(11) \\ 0.57(1) \\ $	N(2)	0.412(1)	0.5198(9)	0.3258(6)	0.0512	C(52)	0.088(1)	-0.210/(7)	0.1003(0)	0.0654
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	N(11) N(12)	0.3/2(1)	0.2988(8)	0.3210(5) 0.3417(6)	0.0330	C(53)	-0.009(1)	-0.199(1)	0.0760(3)	0.0750
$ \begin{array}{c} C12 \\ C13 \\ C13 \\ C149 \\ C13 \\ C149 \\ C141 \\ C140 \\ C15 \\ C141 \\ C15 \\ C141 \\ C15 \\ C15 \\ C141 \\ C15 \\ C15$	C(1)	0.393(1) 0.480(1)	0.2140(9) 0.485(1)	0.3417(0)	0.0402	C(54)	-0.079(1) -0.0880(8)	-0.118(1) -0.0492(9)	0.0750(5)	0.0755
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	C(2)	0.496(1)	0.405(1)	0.3090(3) 0.3983(7)	0.0300	C(56)	-0.009(1)	-0.0614(7)	0.1326(5)	0.0559
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(3)	0.560(1)	0.363(1)	0.4417(1)	0.1041	C(57)	0.256(1)	-0.240(1)	0.1647(8)	0.0551
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	C(4)	0.606(1)	0.412(2)	0.4557(6)	0.1192	C(58)	-0.0093(8)	0.2216(9)	0.1406(5)	0.0466
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	C(5)	0.590(1)	0.498(2)	0.4264(8)	0.0966	C(59)	-0.018(1)	0.1664(7)	0.1075(6)	0.0617
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	C(6)	0.526(1)	0.5350(9)	0.3831(8)	0.0881	C(60)	-0.094(1)	0.202(1)	0.0711(6)	0.0763
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	C(7)	0.384(2)	0.614(1)	0.2953(9)	0.0658	C(61)	-0.161(1)	0.293(1)	0.0678(6)	0.0961
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	C(8)	0.4868(8)	0.1636(7)	0.3696(5)	0.0423	C(62)	-0.153(1)	0.3477(8)	0.1008(7)	0.0911
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	C(9)	0.494(1)	0.0859(8)	0.4081(6)	0.0733	C(63)	-0.077(1)	0.3122(8)	0.1372(6)	0.0764
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	C(10)	0.581(1)	0.0371(7)	0.4361(5)	0.0717	C(64)	0.085(1)	0.243(1)	0.2121(8)	0.0524
$ \begin{array}{cccccc} C(12) & 0.634(9) & 0.144(1) & 0.38 1(6) & 0.032 & C(65) & 0.286(1) & 0.1274(9) & 0.0298(3) & 0.0700 \\ C(14) & 0.325(1) & 0.172(1) & 0.3374(9) & 0.0579 & C(66) & 0.266(1) & 0.216(1) & 0.0042(5) & 0.0804 \\ C(14) & 0.325(1) & 0.172(1) & 0.3374(9) & 0.0579 & C(68) & 0.263(1) & 0.2790(6) & 0.0333(7) & 0.0810 \\ C(15) & 0.184(1) & 0.3252(9) & 0.4304(4) & 0.0472 & C(69) & 0.238(1) & 0.2290(8) & 0.0922(6) & 0.0335 \\ C(16) & 0.1017(8) & 0.3229(9) & 0.4604(6) & 0.0618 & C(70) & 0.3067(9) & 0.1640(9) & 0.1179(4) & 0.0443 \\ C(18) & 0.212(1) & 0.2798(8) & 0.5264(5) & 0.0794 & C(72) & 0.534(1) & -0.0119(7) & 0.1080(5) & 0.0504 \\ C(20) & 0.2796(9) & 0.3024(9) & 0.4547(6) & 0.0611 & C(74) & 0.6812(7) & -0.134(1) & 0.1152(6) & 0.0542 \\ C(21) & 0.1691(9) & 0.5290(7) & 0.4168(5) & 0.0649 & C(75) & 0.619(1) & -0.1814(8) & 0.1722(6) & 0.0932 \\ C(23) & 0.1726(9) & 0.6088(8) & 0.3852(4) & 0.0542 & C(76) & 0.515(1) & -0.1440(8) & 0.1650(6) & 0.0720 \\ C(23) & 0.1726(9) & 0.6088(8) & 0.3852(4) & 0.0542 & C(76) & 0.515(1) & -0.1440(8) & 0.1650(6) & 0.0720 \\ C(24) & 0.1739(9) & 0.6573(8) & 0.4727(6) & 0.0618 & C(79) & 0.2418(8) & -0.0609(7) & 0.0515(5) & 0.0549 \\ C(25) & 0.1704(9) & 0.578(1) & 0.0474(4) & 0.0618 & C(79) & 0.241(1) & -0.1615(9) & -0.0200(5) & 0.0745 \\ C(27) & 0.0335(7) & 0.478(8) & 0.3635(5) & 0.0511 & C(81) & 0.429(1) & -0.1515(8) & -0.0200(5) & 0.0745 \\ C(23) & -0.041(1) & 0.5691(8) & 0.3819(5) & 0.0512 & C(82) & -0.0118(1) & -0.160(9) & 0.0334(6) & 0.0547 \\ C(23) & -0.041(1) & 0.5691(8) & 0.3216(6) & 0.0796 & C(83) & -0.0120(9) & -0.0736(8) & 0.3030(5) & 0.0480 \\ C(31) & -0.955(1) & 0.458(8) & 0.3235(4) & 0.0976 & C(83) & -0.0160(8) & 0.3135(5) & 0.0653 \\ C(34) & 0.4764(8) & 0.3898(8) & 0.0772(6) & 0.0610 & C(88) & -0.118(1) & -0.1747(9) & 0.2385(5) & 0.0654 \\ C(34) & 0.4764(8) & 0.3898(8) & 0.0772(6) & 0.0610 & C(88) & -0.118(1) & -0.0736(8) & 0.3135(5) & 0.0663 \\ C(34) & 0.4764(8) & 0.3898(8) & 0.0772(6) & 0.0610 & C(88) & -0.118(1) & -0.0736(6) & 0.3135(5) & 0.0653 \\ C(34) & 0.4764(8) & 0.3898(8) & 0.0772$	C(11)	0.6615(9)	0.0660(9)	0.4256(6)	0.0699	C(65)	0.3095(9)	0.1013(6)	0.0867(5)	0.0408
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	C(12)	0.6545(9)	0.144(1)	0.38/1(6)	0.0732	C(66)	0.289(1)	0.1274(9)	0.0298(5)	0.0700
$ \begin{array}{c} C(14) \\ (15) \\ (15) \\ (16) \\ (17) \\ (16) \\ (17) \\ (16) \\ (17) \\ (16) \\ (17) \\ (16) \\ (16) \\ (17) \\ (16) \\ (12) \\ (17) \\ (16) \\ (12) \\ (17) \\ (16) \\ (12) \\ (12) \\ (17) \\ (16) \\ (12) \\ (11) \\ $	C(13)	0.567(1)	0.1924(7) 0.172(1)	0.3591(5) 0.3374(0)	0.0591	C(67)	0.200(1) 0.263(1)	0.210(1)	0.0042(5) 0.0352(7)	0.0804
$ \begin{array}{c} C(15) & 0.164(1) & 0.212(9) & 0.4504(6) & 0.06172 & C(25) & 0.2024(5) & 0.2124(5) & 0.0125 \\ C(17) & 0.116(1) & 0.2524(9) & 0.4504(6) & 0.0618 & C(70) & 0.3067(9) & 0.1279(4) & 0.0443 \\ C(17) & 0.116(1) & 0.233(1) & 0.5063(6) & 0.0999 & C(71) & 0.4722(7) & -0.0592(8) & 0.1329(5) & 0.0439 \\ C(19) & 0.224(1) & 0.2232(8) & 0.5006(6) & 0.0772 & C(73) & 0.6382(9) & -0.0494(9) & 0.1152(6) & 0.0646 \\ C(20) & 0.2796(9) & 0.3024(9) & 0.4547(6) & 0.0611 & C(74) & 0.6812(7) & -0.134(1) & 0.1473(6) & 0.0791 \\ C(21) & 0.1691(9) & 0.5290(7) & 0.4168(5) & 0.0459 & C(75) & 0.619(1) & -0.181(48) & 0.1722(6) & 0.0932 \\ C(22) & 0.175(1) & 0.6729(6) & 0.4131(6) & 0.0639 & C(77) & 0.339(1) & -0.0751(7) & 0.0661(4) & 0.0489 \\ C(24) & 0.1739(9) & 0.6573(8) & 0.4727(6) & 0.0518 & C(78) & 0.2438(8) & -0.0609(7) & 0.0515(5) & 0.0549 \\ C(25) & 0.1680(9) & 0.5134(7) & 0.764(5) & 0.0558 & C(80) & 0.334(1) & -0.1615(9) & -0.0200(5) & 0.0756 \\ C(28) & -0.041(1) & 0.5691(8) & 0.335(5) & 0.0512 & C(82) & 0.4311(8) & -0.1232(8) & 0.03077(6) & 0.0547 \\ C(28) & -0.041(1) & 0.5691(8) & 0.3319(6) & 0.0714 & C(83) & -0.0134(7) & 0.2395(5) & 0.0482 \\ C(31) & -0.095(1) & 0.4878(8) & 0.0772(6) & 0.0512 & C(83) & -0.0104(9) & -0.2315(6) & 0.3300(5) & 0.0768 \\ C(33) & -0.1695(8) & 0.5394(1) & 0.3216(6) & 0.0796 & C(85) & -0.0104(1) & -0.2115(6) & 0.0566 \\ C(33) & 0.402(1) & 0.429(1) & -0.2115(6) & 0.0766 \\ C(34) & 0.4764(8) & 0.1235(4) & 0.0477 & C(84) & -0.0438(7) & -0.0635(5) & 0.0482 \\ C(34) & 0.4764(8) & 0.1235(4) & 0.0713 & C(86) & -0.118(1) & -0.1747(9) & 0.2969(6) & 0.0768 \\ C(33) & 0.402(1) & 0.4240(8) & 0.1235(4) & 0.0772 & C(89) & -0.0104(1) & -0.0368(6) & 0.3135(5) & 0.0684 \\ C(34) & 0.4764(8) & 0.1325(4) & 0.0770 & C(87) & -0.1184(9) & -0.0368(6) & 0.3135(5) & 0.0684 \\ C(34) & 0.4764(8) & 0.1325(4) & 0.0477 & C(88) & 0.0104(1) & -0.0562(8) & 0.3773(4) & 0.0566 \\ C(35) & 0.450(1) & 0.4767(9) & 0.134(5) & 0.0695 & C(99) & -0.0263(8) & 0.3135(5) & 0.0684 \\ C(34) & 0.460(1) & 0.246(79) & 0.1384(5) & 0.0697 & C(97) & -0.088(1) & 0.4443(7) $	C(14)	0.525(1) 0.184(1)	0.172(1) 0.3476(7)	0.3374(9) 0.4346(4)	0.0379	C(00)	0.203(1) 0.283(1)	0.2790(0)	0.0333(7)	0.0810
$ \begin{array}{c} c_{107} & 0.161(0) & 0.253(1) & 0.5063(6) & 0.0906 & C(71) & 0.4722(7) & -0.0592(8) & 0.1323(3) & 0.0439 \\ C(18) & 0.212(1) & 0.2078(8) & 0.5264(5) & 0.0794 & C(72) & 0.534(1) & -0.0119(7) & 0.1080(5) & 0.0504 \\ C(20) & 0.2796(9) & 0.3024(9) & 0.4547(6) & 0.0611 & C(74) & 0.6812(7) & -0.134(1) & 0.1473(6) & 0.0791 \\ C(21) & 0.1691(9) & 0.5290(7) & 0.4168(5) & 0.0459 & C(75) & 0.619(1) & -0.1814(8) & 0.1722(6) & 0.0932 \\ C(22) & 0.175(6) & 0.6698(8) & 0.3852(4) & 0.0542 & C(76) & 0.515(1) & -0.1814(8) & 0.1550(6) & 0.0720 \\ C(23) & 0.175(1) & 0.6729(6) & 0.4131(6) & 0.0639 & C(77) & 0.339(1) & -0.0751(7) & 0.0661(4) & 0.0489 \\ C(24) & 0.1739(9) & 0.573(8) & 0.4727(6) & 0.0618 & C(77) & 0.2438(8) & -0.0669(7) & 0.0515(5) & 0.0549 \\ C(25) & 0.1704(9) & 0.578(1) & 0.5044(4) & 0.0618 & C(77) & 0.2438(8) & -0.0669(7) & 0.0515(5) & 0.0765 \\ C(27) & 0.0335(7) & 0.4878(8) & 0.3853(5) & 0.0511 & C(81) & 0.429(1) & -0.1757(8) & -0.0033(5) & 0.0740 \\ C(28) & -0.041(1) & 0.5691(8) & 0.3819(5) & 0.0511 & C(83) & -0.012(9) & -0.0736(8) & 0.0337(6) & 0.0547 \\ C(29) & -0.1428(9) & 0.5999(8) & 0.3706(6) & 0.0747 & C(83) & -0.012(9) & -0.0736(8) & 0.330(5) & 0.0482 \\ C(31) & -0.095(1) & 0.468(1) & 0.3261(6) & 0.0746 & C(83) & -0.010(1) & -0.2115(6) & 0.2864(5) & 0.0662 \\ C(32) & 0.007(1) & 0.4372(7) & 0.3374(6) & 0.0713 & C(86) & -0.113(1) & -0.1737(9) & 0.2899(5) & 0.0482 \\ C(34) & 0.4764(8) & 0.3889(8) & 0.0772(6) & 0.0610 & C(88) & -0.1132(9) & -0.0356(8) & 0.3135(5) & 0.0642 \\ C(34) & 0.4764(8) & 0.3889(8) & 0.0772(6) & 0.0610 & C(88) & -0.113(1) & -0.0562(8) & 0.3135(5) & 0.0652 \\ C(35) & 0.350(1) & 0.476(1) & 0.0120(4) & 0.0750 & C(90) & 0.0420(9) & -0.0356(8) & 0.3135(5) & 0.0652 \\ C(35) & 0.350(1) & 0.476(1) & 0.0120(4) & 0.0750 & C(90) & 0.0420(9) & -0.0368(6) & 0.3135(5) & 0.0652 \\ C(35) & 0.350(1) & 0.478(1) & 0.0150(2) & -0.0726(1) & 0.1482(9) & 0.0572(2) \\ C(34) & 0.458(1) & 0.4381(6) & 0.0572 & C(90) & 0.0420(9) & -0.0356(8) & 0.3137(5) & 0.0520 \\ C(35) & 0.350(1) & 0.478(1) & 0.1257(2) & 0.0573 & C(90) & 0.$	C(15)	0.10+(1)	0.3470(7)	0.4540(4)	0.0472	C(70)	0.205(1)	0.2529(0) 0.1640(9)	0.0922(0) 0.1179(4)	0.0443
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	C(10)	0.116(1)	0.253(1)	0.5063(6)	0.0909	C(71)	0.4722(7)	-0.0592(8)	0.1329(5)	0.0439
$ \begin{array}{cccccc} \hline C(19) & 0.294(1) & 0.2325(8) & 0.5006(6) & 0.0772 & C(73) & 0.6385(9) & -0.0494(9) & 0.1152(6) & 0.0646 \\ \hline C(20) & 0.2796(9) & 0.3024(9) & 0.4547(6) & 0.0611 & C(74) & 0.6812(77) & -0.134(1) & 0.1473(6) & 0.0791 \\ \hline C(21) & 0.1691(9) & 0.5290(7) & 0.4168(5) & 0.0459 & C(77) & 0.619(1) & -0.1814(8) & 0.1722(6) & 0.0932 \\ \hline C(22) & 0.1726(9) & 0.6088(8) & 0.3852(4) & 0.0542 & C(76) & 0.515(1) & -0.1440(8) & 0.1650(6) & 0.0720 \\ \hline C(23) & 0.175(1) & 0.6729(6) & 0.4131(6) & 0.0639 & C(77) & 0.339(1) & -0.0751(7) & 0.0661(4) & 0.0489 \\ \hline C(24) & 0.1739(9) & 0.6573(8) & 0.4727(6) & 0.0639 & C(78) & 0.2481(8) & -0.050(77) & 0.0515(5) & 0.0549 \\ \hline C(25) & 0.1680(9) & 0.5134(7) & 0.4764(5) & 0.0568 & C(80) & 0.334(1) & -0.1615(9) & -0.020(5) & 0.0765 \\ \hline C(27) & 0.0335(7) & 0.4878(8) & 0.3653(5) & 0.0511 & C(81) & 0.429(1) & -0.1757(8) & -0.0035(5) & 0.0746 \\ \hline C(28) & -0.041(1) & 0.5691(8) & 0.3819(5) & 0.0512 & C(82) & -0.0102(9) & -0.0736(8) & 0.303(5) & 0.0480 \\ \hline C(30) & -0.1695(8) & 0.549(1) & 0.3427(6) & 0.0774 & C(84) & -0.0438(7) & -0.1695(8) & 0.337(6) & 0.0747 & C(84) & -0.012(9) & -0.0736(8) & 0.303(5) & 0.0482 \\ \hline C(31) & -0.095(1) & 0.468(1) & 0.3261(6) & 0.0796 & C(85) & -0.010(1) & -0.2115(6) & 0.2864(5) & 0.0607 \\ \hline C(32) & 0.007(1) & 0.4372(7) & 0.3374(6) & 0.0713 & C(86) & -0.118(1) & -0.1747(9) & 0.2969(6) & 0.0768 \\ \hline C(33) & 0.402(1) & 0.420(8) & 0.1235(4) & 0.0497 & C(81) & -0.1182(7) & -0.086(6) & 0.3135(5) & 0.0637 \\ \hline C(33) & 0.450(1) & 0.476(1) & 0.0120(4) & 0.0750 & C(99) & 0.0480(78) & 0.4221(7) & 0.0368(6) \\ \hline C(34) & 0.476(4) & 0.3827(6) & 0.0773 & C(86) & -0.118(3) & -0.086(6) & 0.3135(5) & 0.0658 \\ C(34) & 0.450(1) & 0.476(1) & 0.0120(4) & 0.0750 & C(99) & 0.1092(1) & -0.068(6) & 0.3135(5) & 0.0656 \\ C(35) & 0.350(1) & 0.476(1) & 0.0120(4) & 0.0750 & C(99) & 0.0480(78) & 0.4221(7) & 0.0620 \\ C(33) & 0.552(1) & 0.1746(1) & 0.0658 & C(92) & -0.171(1) & -0.086(6) & 0.3136(5) & 0.0658 \\ C(44) & 0.4890(7) & 0.2127(6) & 0.0658 & C(92) & -0.0263(9) & 0.1032(6) & 0.3140(6) & 0.05$	C(18)	0.212(1)	0.2078(8)	0.5264(5)	0.0794	C(72)	0.534(1)	-0.0119(7)	0.1080(5)	0.0504
$ \begin{array}{c} C(20) \\ C(21) \\ C(21) \\ C(21) \\ O.1591(9) \\ C(22) \\ O.1726(9) \\ O.5290(7) \\ O.4168(5) \\ O.6459 \\ C(75) \\ O.619(1) \\ O.1814(8) \\ O.1724(6) \\ O.1814(8) \\ O.1722(6) \\ O.0932 \\ C(22) \\ O.1726(9) \\ O.688(8) \\ O.3852(4) \\ O.0542 \\ C(75) \\ O.515(1) \\ O.0181(8) \\ O.0057(1) \\ O.0051(1) \\ O.0054(1) \\ O.0054(1) \\ O.0059(7) \\ O.0151(7) \\ O.0051(1) \\ O.0054(1) \\ O.0054(1) \\ O.0059(7) \\ O.0151(5) \\ O.0054(1) \\ O.0054(1) \\ O.0054(1) \\ O.0059(7) \\ O.0151(5) \\ O.0054(1) \\ O.0074(1) \\ O.0056(1) \\ O.0140 \\ C(23) \\ O.007(1) \\ O.457(1) \\ O.056(1) \\ O.0140 \\ C(23) \\ O.007(1) \\ O.457(1) \\ O.0054(1) \\ O.458(1) \\ O.024(1) \\ O.4240(8) \\ O.123(4) \\ O.0760 \\ C(33) \\ O.476(1) \\ O.0120(4) \\ O.0760 \\ C(39) \\ O.0120(7) \\ O.0052(1) \\ O.0173(2) \\ O.0054(1) \\ O.0120(4) \\ O.0760 \\ C(90) \\ O.0420(9) \\ O.0806(1) \\ O.443(7) \\ O.0286(6) \\ O.0132 \\ C(30) \\ O.056(1) \\ O.0173(2) \\ O.005(1) \\ $	C(19)	0.294(1)	0.2325(8)	0.5006(6)	0.0772	C(73)	0.6385(9)	-0.0494(9)	0.1152(6)	0.0646
$ \begin{array}{cccccc} C(21) & 0.1691(9) & 0.5290(7) & 0.4168(5) & 0.0459 & C(75) & 0.619(1) & -0.1814(8) & 0.1722(6) & 0.0932 \\ C(22) & 0.1726(9) & 0.6088(8) & 0.3852(4) & 0.0542 & C(76) & 0.515(1) & -0.1440(8) & 0.1650(6) & 0.0720 \\ C(23) & 0.173(1) & 0.6729(6) & 0.4131(6) & 0.0639 & C(77) & 0.339(1) & -0.0751(7) & 0.0661(4) & 0.0489 \\ C(24) & 0.1739(9) & 0.6573(8) & 0.4727(6) & 0.0639 & C(78) & 0.2438(8) & -0.0609(7) & 0.0515(5) & 0.0549 \\ C(25) & 0.1680(9) & 0.5134(7) & 0.4764(5) & 0.0568 & C(80) & 0.334(1) & -0.1615(9) & -0.0200(5) & 0.0765 \\ C(27) & 0.0335(7) & 0.4878(8) & 0.3653(5) & 0.0511 & C(81) & 0.429(1) & -0.1757(8) & -0.0023(5) & 0.0765 \\ C(27) & 0.0335(7) & 0.4878(8) & 0.3653(5) & 0.0511 & C(81) & 0.429(1) & -0.1757(8) & -0.0023(5) & 0.0740 \\ C(28) & -0.041(1) & 0.5691(8) & 0.3819(5) & 0.0512 & C(82) & 0.4311(8) & -0.1325(8) & 0.0377(6) & 0.0547 \\ C(29) & -0.1428(9) & 0.5999(8) & 0.3706(6) & 0.0740 & C(83) & -0.0102(9) & -0.0736(8) & 0.3030(5) & 0.0480 \\ C(30) & -0.1695(8) & 0.549(1) & 0.3261(6) & 0.0774 & C(84) & -0.0438(7) & -0.1609(8) & 0.2895(5) & 0.0482 \\ C(31) & -0.095(1) & 0.468(1) & 0.3261(6) & 0.0713 & C(86) & -0.118(1) & -0.1747(9) & 0.2969(6) & 0.0768 \\ C(33) & 0.402(1) & 0.4372(7) & 0.3374(6) & 0.0713 & C(86) & -0.118(1) & -0.1747(9) & 0.2969(6) & 0.0768 \\ C(34) & 0.4764(8) & 0.3898(8) & 0.0772(6) & 0.0610 & C(88) & -0.118(3)9 & -0.0368(6) & 0.3135(5) & 0.0653 \\ C(35) & 0.450(1) & 0.4157(9) & 0.0214(5) & 0.0760 & C(89) & -0.118(3)9 & -0.0368(6) & 0.3135(5) & 0.0652 \\ C(36) & 0.550(1) & 0.476(6) & 0.1953(5) & 0.0441 & C(93) & 0.227(1) & -0.086(1) & 0.4424(7) & 0.0928 \\ C(40) & 0.540(1) & 0.2426(9) & 0.0583(7) & 0.0678 & C(91) & 0.068(1) & -0.1079(9) & 0.4779(5) & 0.0732 \\ C(33) & 0.532(29) & 0.2746(6) & 0.1953(5) & 0.0541 & C(93) & 0.227(1) & -0.086(1) & 0.4443(7) & 0.0928 \\ C(40) & 0.540(1) & 0.2467(9) & 0.1843(5) & 0.0695 & C(95) & -0.0263(9) & 0.1326(6) & 0.3140(6) & 0.552 \\ C(42) & 0.661(1) & 0.0919(6) & 0.0916(5) & C(95) & -0.0263(9) & 0.1326(6) & 0.378(6) & 0.0732 \\ C(44) & 0.539(1) & 0.31$	C(20)	0.2796(9)	0.3024(9)	0.4547(6)	0.0611	C(74)	0.6812(7)	-0.134(1)	0.1473(6)	0.0791
$\begin{array}{cccccc} C(22) & 0.1726(9) & 0.6088(8) & 0.3852(4) & 0.0542 & C(76) & 0.515(1) & -0.1440(8) & 0.1650(6) & 0.0720 \\ C(23) & 0.175(1) & 0.6729(6) & 0.4131(6) & 0.0639 & C(77) & 0.339(1) & -0.0751(7) & 0.0661(4) & 0.0489 \\ C(24) & 0.1739(9) & 0.6573(8) & 0.4727(6) & 0.0639 & C(78) & 0.2438(8) & -0.0609(7) & 0.0515(5) & 0.0549 \\ C(25) & 0.1704(9) & 0.578(1) & 0.5044(4) & 0.0618 & C(79) & 0.241(1) & -0.1040(9) & 0.0084(6) & 0.0597 \\ C(26) & 0.1680(9) & 0.5134(7) & 0.4764(5) & 0.0568 & C(80) & 0.334(1) & -0.1615(9) & -0.0200(5) & 0.0765 \\ C(27) & 0.0335(7) & 0.4878(8) & 0.3653(5) & 0.0531 & C(81) & 0.429(1) & -0.1757(8) & -0.0053(5) & 0.0740 \\ C(28) & -0.041(1) & 0.5691(8) & 0.3819(5) & 0.0512 & C(82) & 0.431(8) & -0.1325(8) & 0.0377(6) & 0.0547 \\ C(29) & -0.1428(9) & 0.5999(8) & 0.3706(6) & 0.0747 & C(84) & 0.0438(7) & -0.1609(8) & 0.2895(5) & 0.0482 \\ C(30) & -0.1695(8) & 0.549(1) & 0.3427(6) & 0.0747 & C(84) & -0.012(9) & -0.0736(8) & 0.3030(5) & 0.0480 \\ C(30) & -0.1695(8) & 0.549(1) & 0.3427(6) & 0.0713 & C(85) & -0.010(1) & -0.2115(6) & 0.2864(5) & 0.0607 \\ C(32) & 0.007(1) & 0.4372(7) & 0.3374(6) & 0.0713 & C(86) & -0.118(1) & -0.1747(9) & 0.2869(6) & 0.0768 \\ C(33) & 0.402(1) & 0.4240(8) & 0.1235(4) & 0.0497 & C(87) & -0.172(7) & -0.087(1) & 0.3105(6) & 0.0684 \\ C(34) & 0.4764(4) & 0.3898(8) & 0.0772(6) & 0.0610 & C(88) & -0.118(9) & -0.0368(6) & 0.3135(5) & 0.0635 \\ C(35) & 0.450(1) & 0.4157(9) & 0.0214(5) & 0.0760 & C(89) & 0.109(1) & -0.0562(8) & 0.3173(4) & 0.0566 \\ C(36) & 0.350(1) & 0.475(1) & 0.0120(4) & 0.0750 & C(90) & 0.042(9) & -0.0807(8) & 0.4221(7) & 0.0620 \\ C(37) & 0.2753(9) & 0.5998(9) & 0.0583(7) & 0.0878 & C(91) & 0.068(1) & -0.1079(9) & 0.4779(5) & 0.0732 \\ C(36) & 0.3104(0) & 0.4789(1) & 0.1845(7) & 0.0695 & C(92) & 0.160(2) & -0.111(1) & 0.4890(5) & 0.0910 \\ C(39) & 0.352(2) & 0.274(6) & 0.1953(5) & 0.0695 & C(92) & -0.026(1) & 0.0326(6) & 0.3256(7) & 0.0712 \\ C(44) & 0.637(1) & 0.557(1) & 0.1842(6) & 0.0695 & C(95) & -0.0263(9) & 0.1426(9) & 0.3258(5) & 0.0752 \\ C(44) & 0.637(1) & 0.5$	C(21)	0.1691(9)	0.5290(7)	0.4168(5)	0.0459	C(75)	0.619(1)	-0.1814(8)	0.1722(6)	0.0932
$\begin{array}{ccccccc} C(23) & 0.175(1) & 0.6729(6) & 0.4131(6) & 0.0639 & C(77) & 0.339(1) & -0.0751(7) & 0.0661(4) & 0.0489 \\ C(24) & 0.1739(9) & 0.6573(8) & 0.4727(6) & 0.0639 & C(78) & 0.243(8) & -0.0609(7) & 0.0515(5) & 0.0549 \\ C(25) & 0.1704(9) & 0.578(1) & 0.5044(4) & 0.0618 & C(79) & 0.241(1) & -0.1040(9) & 0.0084(6) & 0.0597 \\ C(26) & 0.0335(7) & 0.478(8) & 0.3653(5) & 0.0531 & C(81) & 0.429(1) & -0.1757(8) & -0.0053(5) & 0.0746 \\ C(23) & -0.041(1) & 0.5691(8) & 0.3819(5) & 0.0512 & C(81) & 0.429(1) & -0.1757(8) & -0.0053(5) & 0.0747 \\ C(29) & -0.1428(9) & 0.5999(8) & 0.3706(6) & 0.0740 & C(83) & -0.0102(9) & -0.0736(8) & 0.3030(5) & 0.0480 \\ C(30) & -0.1695(8) & 0.549(1) & 0.3427(6) & 0.0747 & C(84) & 0.0438(7) & -0.1609(8) & 0.2895(5) & 0.0482 \\ C(31) & -0.095(1) & 0.468(1) & 0.3261(6) & 0.0796 & C(85) & -0.010(1) & -0.2115(6) & 0.2864(5) & 0.0607 \\ C(32) & 0.007(1) & 0.4372(7) & 0.3374(6) & 0.0713 & C(86) & -0.118(1) & -0.1747(9) & 0.2969(6) & 0.0768 \\ C(33) & 0.402(1) & 0.4240(8) & 0.125(4) & 0.0497 & C(87) & -0.1725(7) & -0.087(1) & 0.3105(6) & 0.0684 \\ C(34) & 0.4764(8) & 0.3898(8) & 0.0772(6) & 0.0610 & C(88) & -0.1183(9) & -0.0562(8) & 0.3135(5) & 0.0635 \\ C(36) & 0.350(1) & 0.475(1) & 0.0120(4) & 0.0750 & C(90) & 0.0420(9) & -0.087(8) & 0.4221(7) & 0.0620 \\ C(37) & 0.2753(9) & 0.598(9) & 0.0583(7) & 0.0878 & C(91) & 0.068(1) & -0.1079(9) & 0.4779(5) & 0.0732 \\ C(38) & 0.3013(9) & 0.4839(9) & 0.1141(5) & 0.0658 & C(92) & 0.160(2) & -0.111(1) & 0.4880(5) & 0.0912 \\ C(40) & 0.640(1) & 0.2467(9) & 0.1843(5) & 0.0699 & C(94) & 0.227(1) & -0.086(1) & 0.4443(7) & 0.0928 \\ C(44) & 0.640(1) & 0.2467(9) & 0.1843(5) & 0.0699 & C(94) & 0.201(1) & -0.059(1) & 0.3485(6) & 0.0385 \\ C(44) & 0.640(1) & 0.2467(9) & 0.1843(5) & 0.0699 & C(94) & 0.201(1) & -0.086(1) & 0.4443(7) & 0.0928 \\ C(44) & 0.640(1) & 0.2467(9) & 0.1843(5) & 0.0699 & C(95) & -0.0263(9) & 0.1032(6) & 0.3140(6) & 0.0552 \\ C(44) & 0.640(1) & 0.2467(9) & 0.1843(5) & 0.0699 & C(95) & -0.0263(9) & 0.1032(6) & 0.3485(6) & 0.0673 \\ C(44) & 0.569(1) & 0.581($	C(22)	0.1726(9)	0.6088(8)	0.3852(4)	0.0542	C(76)	0.515(1)	-0.1440(8)	0.1650(6)	0.0720
$\begin{array}{cccccc} C(24) & 0.1739(9) & 0.6573(8) & 0.4727(6) & 0.0639 & C(78) & 0.2438(8) & -0.0609(7) & 0.0515(5) & 0.0549 \\ C(25) & 0.1704(9) & 0.578(1) & 0.5044(4) & 0.0618 & C(79) & 0.241(1) & -0.1615(9) & -0.0200(5) & 0.0765 \\ C(27) & 0.0335(7) & 0.4878(8) & 0.3653(5) & 0.0531 & C(81) & 0.429(1) & -0.1757(8) & -0.0053(5) & 0.0740 \\ C(28) & -0.041(1) & 0.5691(8) & 0.3819(5) & 0.0512 & C(82) & 0.4311(8) & -0.1325(8) & 0.0337(6) & 0.0547 \\ C(29) & -0.1428(9) & 0.5999(8) & 0.3706(6) & 0.0740 & C(83) & -0.0102(9) & -0.0736(8) & 0.3030(5) & 0.0480 \\ C(30) & -0.1695(8) & 0.549(1) & 0.3427(6) & 0.0747 & C(84) & 0.0438(7) & -0.1609(8) & 0.2895(5) & 0.0482 \\ C(31) & -0.095(1) & 0.468(1) & 0.3261(6) & 0.0747 & C(85) & -0.010(1) & -0.2115(6) & 0.2864(5) & 0.0607 \\ C(32) & 0.007(1) & 0.4372(7) & 0.3374(6) & 0.0713 & C(86) & -0.118(1) & -0.1747(9) & 0.2969(6) & 0.0768 \\ C(33) & 0.402(1) & 0.4240(8) & 0.1235(4) & 0.0497 & C(87) & -0.0172(7) & -0.087(1) & 0.3135(5) & 0.0635 \\ C(35) & 0.450(1) & 0.4157(9) & 0.0214(5) & 0.0760 & C(89) & 0.109(1) & -0.0562(8) & 0.3135(5) & 0.0635 \\ C(36) & 0.350(1) & 0.476(1) & 0.0120(4) & 0.0750 & C(90) & 0.0420(9) & -0.087(8) & 0.3217(4) & 0.0566 \\ C(36) & 0.350(1) & 0.476(1) & 0.0120(4) & 0.0750 & C(90) & 0.0420(9) & -0.087(8) & 0.3140(6) & 0.0532 \\ C(33) & 0.3013(9) & 0.4839(9) & 0.1141(5) & 0.0658 & C(92) & 0.160(2) & -0.111(1) & 0.44890(5) & 0.0713 \\ C(38) & 0.3013(9) & 0.4839(9) & 0.1843(5) & 0.0658 & C(92) & 0.160(2) & -0.111(1) & 0.4880(5) & 0.0732 \\ C(44) & 0.640(1) & 0.2467(9) & 0.1843(5) & 0.0659 & C(95) & -0.0263(9) & 0.1322(6) & 0.3140(6) & 0.0552 \\ C(42) & 0.661(1) & 0.0919(6) & 0.1991(6) & 0.0684 & C(96) & -0.099(1) & 0.1492(9) & 0.2757(5) & 0.0520 \\ C(44) & 0.4890(7) & 0.2112(9) & 0.2082(5) & 0.0515 & C(98) & -0.1711(9) & 0.2386(6) & 0.0573 \\ C(44) & 0.4890(7) & 0.2112(9) & 0.2082(5) & 0.0515 & C(98) & -0.1711(9) & 0.238(6) & 0.0573 \\ C(44) & 0.4890(7) & 0.2112(9) & 0.2082(5) & 0.0515 & C(99) & -0.0263(9) & 0.1322(6) & 0.345(7) & 0.0713 \\ C(44) & 0.580(1) & 0.4340(7) & 0.229(5) & 0$	C(23)	0.175(1)	0.6729(6)	0.4131(6)	0.0639	C(77)	0.339(1)	-0.0751(7)	0.0661(4)	0.0489
$ \begin{array}{c} C(25) & 0.1704(9) & 0.578(1) & 0.5044(4) & 0.0618 & C(79) & 0.241(1) & -0.1619(9) & 0.0084(6) & 0.0597 \\ C(26) & 0.1680(9) & 0.5134(7) & 0.4764(5) & 0.0568 & C(80) & 0.334(1) & -0.1615(9) & -0.0020(5) & 0.0746 \\ C(28) & -0.041(1) & 0.5691(8) & 0.3819(5) & 0.0512 & C(82) & 0.4311(8) & -0.1325(8) & 0.0377(6) & 0.0547 \\ C(29) & -0.1428(9) & 0.5999(8) & 0.3706(6) & 0.0740 & C(83) & -0.0102(9) & -0.0736(8) & 0.3030(5) & 0.0480 \\ C(30) & -0.1695(8) & 0.549(1) & 0.3427(6) & 0.0747 & C(84) & 0.0438(7) & -0.1609(8) & 0.2895(5) & 0.0482 \\ C(31) & -0.095(1) & 0.468(1) & 0.3261(6) & 0.0796 & C(85) & -0.010(1) & -0.2115(6) & 0.2864(5) & 0.0607 \\ C(32) & 0.007(1) & 0.4372(7) & 0.3374(6) & 0.0713 & C(86) & -0.118(1) & -0.1747(9) & 0.2969(6) & 0.0768 \\ C(33) & 0.402(1) & 0.44240(8) & 0.1235(4) & 0.0497 & C(87) & -0.1725(7) & -0.087(1) & 0.3105(6) & 0.0654 \\ C(34) & 0.4764(8) & 0.3898(8) & 0.0772(6) & 0.0610 & C(88) & -0.1183(9) & -0.0368(6) & 0.3135(5) & 0.0635 \\ C(35) & 0.450(1) & 0.4157(9) & 0.0214(5) & 0.0760 & C(89) & 0.109(1) & -0.0562(8) & 0.3773(4) & 0.0566 \\ C(36) & 0.350(1) & 0.4457(9) & 0.0120(4) & 0.0750 & C(90) & 0.0420(9) & -0.0807(8) & 0.4221(7) & 0.0620 \\ C(39) & 0.5322(9) & 0.2746(6) & 0.1953(7) & 0.0658 & C(92) & 0.160(2) & -0.111(1) & 0.4890(5) & 0.0910 \\ C(39) & 0.5322(9) & 0.2746(6) & 0.1953(5) & 0.0658 & C(92) & 0.160(2) & -0.111(1) & 0.4890(5) & 0.0910 \\ C(39) & 0.5322(9) & 0.2746(6) & 0.1953(5) & 0.0454 & C(95) & -0.0263(9) & 0.1032(6) & 0.3140(6) & 0.0552 \\ C(44) & 0.661(1) & 0.0919(6) & 0.1843(5) & 0.0695 & C(95) & -0.0263(9) & 0.1032(6) & 0.3140(6) & 0.0552 \\ C(44) & 0.661(1) & 0.0191(6) & 0.0684 & C(96) & -0.099(1) & 0.1382(6) & 0.0326(7) & 0.0711 \\ C(48) & 0.535(1) & 0.1184(57) & 0.0851 & C(99) & -0.098(1) & 0.232(6) & 0.3140(6) & 0.0552 \\ C(44) & 0.569(1) & 0.518(8) & 0.1484(7) & 0.0821 & C(100)^{r} & -0.098(1) & 0.2326(7) & 0.0711 \\ C(48) & 0.567(1) & 0.198(6) & 0.0697 & C(200)^{r} & -0.098(1) & 0.232(1) & 0.3648(5) & 0.0759 \\ C(44) & 0.569(1) & 0.518(8) & 0.1484(7) & 0.0821 & C(100)^{r} &$	C(24)	0.1739(9)	0.6573(8)	0.4727(6)	0.0639	C(78)	0.2438(8)	-0.0609(7)	0.0515(5)	0.0549
$ \begin{array}{c} C(26) & 0.1680(9) & 0.5134(7) & 0.4704(3) & 0.0508 & C(80) & 0.534(1) & -0.1615(9) & -0.0203(5) & 0.0740 \\ C(28) & -0.041(1) & 0.5691(8) & 0.3819(5) & 0.0512 & C(82) & 0.4311(8) & -0.1325(8) & -0.0053(5) & 0.0547 \\ C(29) & -0.1428(9) & 0.5999(8) & 0.3706(6) & 0.0740 & C(83) & -0.0102(9) & -0.0736(8) & 0.3030(5) & 0.0480 \\ C(30) & -0.1695(8) & 0.549(1) & 0.3427(6) & 0.0747 & C(84) & 0.0438(7) & -0.1690(8) & 0.2895(5) & 0.0642 \\ C(31) & -0.095(1) & 0.468(1) & 0.3261(6) & 0.0796 & C(85) & -0.010(1) & -0.2115(6) & 0.2864(5) & 0.0607 \\ C(23) & 0.007(1) & 0.4372(7) & 0.3374(6) & 0.0713 & C(86) & -0.118(1) & -0.1747(9) & 0.2969(6) & 0.0768 \\ C(33) & 0.402(1) & 0.4240(8) & 0.1235(4) & 0.0497 & C(87) & -0.1725(7) & -0.087(1) & 0.3105(6) & 0.0684 \\ C(34) & 0.4764(8) & 0.3898(8) & 0.0772(6) & 0.0610 & C(88) & -0.118(3)9 & -0.0368(6) & 0.3135(5) & 0.0635 \\ C(35) & 0.450(1) & 0.476(1) & 0.0120(4) & 0.0750 & C(90) & 0.0420(9) & -0.087(8) & 0.422(17) & 0.0566 \\ C(36) & 0.350(1) & 0.476(1) & 0.0120(4) & 0.0758 & C(91) & 0.068(1) & -0.1079(9) & 0.4779(5) & 0.0732 \\ C(38) & 0.3013(9) & 0.4839(9) & 0.0583(7) & 0.0878 & C(91) & 0.068(1) & -0.1079(9) & 0.4779(5) & 0.0732 \\ C(40) & 0.640(1) & 0.2467(9) & 0.1843(5) & 0.0609 & C(94) & 0.201(1) & -0.059(1) & 0.3885(6) & 0.0868 \\ C(41) & 0.7040(7) & 0.155(1) & 0.1862(6) & 0.0695 & C(95) & -0.0263(9) & 0.1032(6) & 0.3140(6) & 0.0552 \\ C(42) & 0.661(1) & 0.0919(6) & 0.0599 & C(97) & -0.1711(9) & 0.2366(9) & 0.2820(6) & 0.0673 \\ C(44) & 0.4890(7) & 0.2112(9) & 0.208(5) & 0.0515 & C(98) & -0.171(1) & 0.2781(6) & 0.3255(7) & 0.0711 \\ C(45) & 0.5205(9) & 0.4580(8) & 0.1847(6) & 0.0559 & C(97) & -0.1711(9) & 0.2366(9) & 0.2820(6) & 0.0673 \\ C(44) & 0.4890(7) & 0.212(9) & 0.028(5) & 0.0515 & C(98) & -0.171(1) & 0.2781(6) & 0.3255(7) & 0.0711 \\ C(45) & 0.588(1) & 0.4143(6) & 0.0863 & C(200)^c & 0.993(3) & 0.561(2) & 0.1740(2) & 0.3287(7) & 0.176(7)^c \\ C(46) & 0.588(1) & 0.4143(6) & 0.0863 & C(1200)^c & 0.993(3) & 0.561(2) & 0.177(2) & 0.06(1)^c \\ C(49) & 0.569(1) & 0.5813(8) & 0.1443(6)$	C(25)	0.1704(9)	0.578(1)	0.5044(4)	0.0618	C(79)	0.241(1)	-0.1040(9)	0.0084(6)	0.0597
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(20)	0.1080(9)	0.5154(7)	0.4704(3) 0.2652(5)	0.0508	C(80)	0.334(1) 0.429(1)	-0.1013(9) -0.1757(9)	-0.0200(3) -0.0053(5)	0.0703
$\begin{array}{c} C(29) & -0.1428(9) & 0.5999(8) & 0.3706(6) & 0.0742 & C(82) & -0.01716(9) & -0.0736(8) & 0.330(6) & 0.08480 \\ C(30) & -0.1695(8) & 0.549(1) & 0.3427(6) & 0.0747 & C(84) & 0.04438(7) & -0.1609(8) & 0.2895(5) & 0.0482 \\ C(31) & -0.095(1) & 0.468(1) & 0.3261(6) & 0.0796 & C(85) & -0.010(1) & -0.2115(6) & 0.2864(5) & 0.0607 \\ C(32) & 0.007(1) & 0.4372(7) & 0.3374(6) & 0.0713 & C(86) & -0.118(1) & -0.1747(9) & 0.2969(6) & 0.0768 \\ C(33) & 0.402(1) & 0.4240(8) & 0.1235(4) & 0.0497 & C(87) & -0.1725(7) & -0.087(1) & 0.3105(6) & 0.0684 \\ C(34) & 0.4764(8) & 0.3898(8) & 0.0772(6) & 0.0610 & C(88) & -0.1183(9) & -0.0368(6) & 0.3135(5) & 0.0635 \\ C(35) & 0.450(1) & 0.4157(9) & 0.0214(5) & 0.0760 & C(89) & 0.109(1) & -0.0562(8) & 0.3773(4) & 0.0566 \\ C(36) & 0.350(1) & 0.476(1) & 0.0120(4) & 0.0750 & C(90) & 0.0420(9) & -0.0807(8) & 0.4221(7) & 0.0620 \\ C(37) & 0.2753(9) & 0.5998(9) & 0.0583(7) & 0.0878 & C(91) & 0.068(1) & -0.1079(9) & 0.4779(5) & 0.0732 \\ C(38) & 0.3013(9) & 0.4839(9) & 0.1141(5) & 0.0658 & C(92) & 0.160(2) & -0.111(1) & 0.4890(5) & 0.0910 \\ C(39) & 0.5322(9) & 0.2746(6) & 0.1953(5) & 0.0441 & C(93) & 0.227(1) & -0.086(1) & 0.4443(7) & 0.0928 \\ C(40) & 0.640(1) & 0.2467(9) & 0.1843(5) & 0.0609 & C(94) & 0.201(1) & -0.059(1) & 0.3885(6) & 0.0868 \\ C(42) & 0.661(1) & 0.0919(6) & 0.0599 & C(95) & -0.0263(9) & 0.1032(6) & 0.03552 \\ C(42) & 0.661(1) & 0.0919(6) & 0.0599 & C(95) & -0.0263(9) & 0.1032(6) & 0.3552 \\ C(44) & 0.4890(7) & 0.2112(9) & 0.2282(5) & 0.0515 & C(98) & -0.171(1) & 0.2781(6) & 0.3256(7) & 0.0711 \\ C(45) & 0.520(9) & 0.4580(8) & 0.1897(6) & 0.0459 & C(99) & -0.098(1) & 0.232(1) & 0.3688(5) & 0.0759 \\ C(44) & 0.4580(7) & 0.2112(9) & 0.2273(6) & 0.0657 & C(200)^c & 0.993(3) & 0.561(2) & 0.177(2) & 0.06(1)^c \\ C(44) & 0.4580(7) & 0.557(1) & 0.1845(7) & 0.0821 & C(200)^c & 0.993(3) & 0.561(2) & 0.177(2) & 0.06(1)^c \\ C(45) & 0.558(1) & 0.3316(9) & 0.1469(5) & 0.0638 & C(300)^c & 0.592(2) & 0.744(2) & 0.338(5) & 0.0728 \\ C(47) & 0.569(1) & 0.5813(8) & 0.1443(6) & 0.0840 & C(202)^c & 0.889$	C(27)	-0.0333(7)	0.4678(8)	0.3033(5)	0.0512	C(81)	0.429(1) 0.4311(8)	-0.1325(8)	0.0035(5) 0.0377(6)	0.0740
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(20)	-0.1428(9)	0.5999(8)	0.3706(6)	0.0740	C(82)	-0.0102(9)	-0.0736(8)	0.3030(5)	0.0480
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(30)	-0.1695(8)	0.549(1)	0.3427(6)	0.0747	C(84)	0.0438(7)	-0.1609(8)	0.2895(5)	0.0482
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(31)	-0.095(1)	0.468(1)	0.3261(6)	0.0796	C(85)	-0.010(1)	-0.2115(6)	0.2864(5)	0.0607
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(32)	0.007(1)	0.4372(7)	0.3374(6)	0.0713	C(86)	-0.118(1)	-0.1747(9)	0.2969(6)	0.0768
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(33)	0.402(1)	0.4240(8)	0.1235(4)	0.0497	C(87)	-0.1725(7)	-0.087(1)	0.3105(6)	0.0684
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(34)	0.4764(8)	0.3898(8)	0.0772(6)	0.0610	C(88)	-0.1183(9)	-0.0368(6)	0.3135(5)	0.0635
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(35)	0.450(1)	0.4157(9)	0.0214(5)	0.0760	C(89)	0.109(1)	-0.0562(8)	0.3773(4)	0.0566
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(36)	0.350(1)	0.476(1)	0.0120(4)	0.0750	C(90)	0.0420(9)	-0.0807(8)	0.4221(7)	0.0620
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(37)	0.2753(9)	0.5098(9)	0.0583(7)	0.0878	C(91)	0.068(1) 0.160(2)	-0.10/9(9)	0.4779(5)	0.0732
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(38)	0.3013(9)	0.4839(9)	0.1141(3) 0.1052(5)	0.0038	C(92)	0.100(2) 0.227(1)	-0.086(1)	0.4690(3) 0.4442(7)	0.0910
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(39)	0.5522(9) 0.640(1)	0.2740(0) 0.2467(9)	0.1933(3) 0.1843(5)	0.0441	C(93)	0.227(1) 0.201(1)	-0.080(1) -0.059(1)	0.4445(7)	0.0928
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(40) C(41)	0.040(1)	0.2407(9)	0.1843(5) 0.1862(6)	0.0695	C(95)	-0.0263(9)	0.032(6)	0.3140(6)	0.0552
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(42)	0.661(1)	0.0919(6)	0.1991(6)	0.0684	C(96)	-0.099(1)	0.1492(9)	0.2757(5)	0.0520
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(43)	0.553(1)	0.1198(7)	0.2100(5)	0.0599	C(97)	-0.1711(9)	0.2366(9)	0.2820(6)	0.0673
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(44)	0.4890(7)	0.2112(9)	0.2082(5)	0.0515	C(98)	-0.171(1)	0.2781(6)	0.3265(7)	0.0711
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(45)	0.5205(9)	0.4580(8)	0.1897(6)	0.0469	C(99)	-0.098(1)	0.232(1)	0.3648(5)	0.0759
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	C(46)	0.588(1)	0.4340(7)	0.2299(5)	0.0537	C(100)	-0.026(1)	0.1446(9)	0.3585(5)	0.0728
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(47)	0.6462(9)	0.484(1)	0.2273(6)	0.0697	C(200) ^c	0.993(3)	0.561(2)	0.177(2)	$0.06(1)^{e}$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(48)	0.637(1)	0.557(1)	0.1845(7)	0.0821	Cl(201) ^c	0.997(2)	0.524(1)	0.119(1)	0.208(8) ^e
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	C(49)	0.569(1)	0.5813(8)	0.1443(6)	0.0840	CI(202) ^c	0.889(1)	0.650(1)	0.1943(7)	$0.148(6)^{e}$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(50)	0.511(1)	0.5316(9)	0.1469(5)	0.0638	CI(300)°	0.502(3)	0.842(3)	0.335(2)	$0.08(1)^{e}$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	MO(51)	0.2007(1)	-0.01/38(9)	0.212/9(0)	0.0394	CI(301) ^e	0.300(2)	0.093(1)	0.3387(9)	0.170(7)*
P(51) = 0.3363(3) = -0.0144(3) = 0.1235(2) = 0.00553 = C1(305) = 0.515(2) = 0.700(2) = 0.591(1) = 0.115(8)	Cl(51)	0.2704(4)	-0.16397(3)	0.2572(2) 0.2672(2)	0.0305	C1(302)*	0.575(2) 0.515(2)	0.7 + (2) 0.760(2)	0.320(1)	$0.102(0)^{2}$
	P(51)	0.3363(3)	-0.0144(3)	0.1235(2)	0.0453	CI(303)"	0.513(2)	0.700(2)	0.271(1)	0.115(0)

^a Estimated standard deviations in the least significant digits are given in parentheses. ^b $U(eq) = [U(11) \cdot U(22) \cdot U(33)]^{1/3}$. ^c Occupancy factor 0.5. ^d Occupancy factor 0.25. ^e U(iso).

hedral geometry with trans-phosphine ligands. Then, a virtual triplet^{27,36,37} was expected for the ¹H NMR spectra of complexes 5 and 6, which contain trans-PMePh₂ ligands, and those of complexes 7 and 8, which contain PMe₂Ph ligands. Indeed, the spectrum of complex 5 exhibits a pseudotriplet centered at

2.38 ppm but also two doublets at 2.20 and 1.63 ppm, which indicates partial dissociation of 5 into PMePh₂ and a fivecoordinated species. On the other hand, that of complex 6 shows two virtual triplets, in relative intensities 4:1, centered at 2.37 and 2.31 ppm, which are assigned to the methyl proton resonances of the phosphines, and three singlets at 3.21, 3.19, and 3.02 ppm, which arise from the methyl proton resonances of the hydrazido ligands. The signals at 3.19 and 2.37 ppm

Crabtree, R. H. Organometallic Chemistry of the Transition Metals; (36) Wiley: New York, 1988; pp 212-217.
(37) Ali, H. M.; Leigh, G. J. J. Chem. Soc., Dalton Trans. 1986, 213.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $[Mo(NNPh_2)_2Cl_2(PPh_3)]$

_				
	Mo(1) - Cl(1)	2,448(4)	Mo(51) - Cl(51)	2.454(4)
	Mo(1) - Cl(2)	2.384(3)	Mo(51) - Cl(52)	2.383(3)
:	Mo(1) - P(1)	2.526(4)	Mo(51) - P(51)	2.537(4)
	Mo(1) - N(1)	1.76(1)	Mo(51) - N(51)	1.75(1)
	Mo(1) - N(11)	1.76(1)	Mo(51)-N(61)	1.75(1)
	P(1) - C(25)	1.820(6)	P(51)-C(87)	1.840(7)
	P(1) - C(31)	1.824(8)	P(51) - C(75)	1.827(6)
	P(1) - C(37)	1.840(8)	P(51)-C(81)	1.825(7)
•	N(1) - N(2)	1.33(1)	N(51)-N(52)	1.33(1)
	N(2) - C(1)	1.43(1)	N(52) - C(51)	1.41(1)
	N(2) - C(7)	1.41(1)	N(52)-C(57)	1.44(1)
	N(11) - N(12)	1.30(1)	N(61) - N(62)	1.34(1)
	N(12) - C(13)	1.45(1)	N(62) - C(63)	1.43(1)
	N(12) - C(19)	1.45(1)	N(62) - C(69)	1.41(1)
C 1	$(2) = M_{2}(1) = C_{1}(1)$	92 0(1)	$C_{1}(52) = M_{2}(51) = C_{1}(51)$) 94 5 (1)
	(2) = Mo(1) = CI(1)	161.2(1)	P(51) = Mo(51) = Cl(51)	1665(1)
r(D/	1) = MO(1) = CI(1) 1) = Mo(1) = CI(2)	$\frac{101.3(1)}{92.4(1)}$	P(51) = MO(51) = CI(51) P(51) = Mo(51) = CI(52)	82.2(1)
F (NT/	(1) = Mo(1) = CI(2)	03.4(1)	$F(51) = M_0(51) = CI(52)$	02.3(1)
LN (NT/	(1) = Mo(1) = CI(1)	$\frac{92.3(3)}{125.0(3)}$	N(51) = Mo(51) = CI(51)	1226(3)
LN (NT/	(1) - Mo(1) - CI(2)	123.0(3)	N(51) - Mo(51) - CI(52)	122.0(3)
1 N (NT/	(1) - Mo(1) - F(1)	90.7(3)	N(51) - Mo(51) - F(51)	95.0(3)
NT/	$(11) = M_0(1) = C(1)$	1107(3)	$N(61) = M_0(51) = C1(51)$	1221(3)
NI($(11)^{-1}$ MO(1) $-C(2)$	0/3(3)	N(01) = MO(51) = CI(52) N(61) = MO(51) = D(51)	122.1(3)
NI/	(11) - Mo(1) - N(1)	115 2(4)	$N(61) = M_0(51) = N(51)$	1153(4)
14((1) - WO(1) - N(1)	113.2(4)	$I_{(01)} = I_{(01)} $	115.5(4)
N(2)-N(1)-Mo(1)	176.8(8)	N(52) - N(51) - Mo(51)	172.7(8)
C(1) - N(2) - N(1)	120.6(10)	C(51) - N(52) - N(51)	121.2(9)
C((7) - N(2) - N(1)	115.6(10)	C(57) - N(52) - N(51)	117.2(9)
C(7) - N(2) - C(1)	123.6(9)	C(57) - N(52) - C(51)	121.6(9)
N((12) - N(11) - Mo(1)	172.9(9)	N(62) - N(61) - Mo(51)	169.3(8)
C(13) - N(12) - N(11)	119.8(10)	C(63) = N(62) = N(61)	118.2(9)
C(19)-N(12)-N(11)	120.2(9)	C(69) = N(62) = N(61)	118.6(9)
C(19)-N(12)-C(13)	119.5(9)	C(69) = N(62) = C(63)	123.0(9)

have the same integrated intensity, while the sum of the intensities of the signals at 3.21 and 3.02 equals the intensity of the signal at 2.31 ppm. This is consistent with a 4:1 mixture of two isomers A and B, which respectively display equivalent and inequivalent hydrazido-methyl groups. Actually there are two possible isomers A and A' with equivalent hydrazido ligands (see Chart 1); it is noteworthy that arrangement A (outer methyl groups) is found in the solid-state structure of 4, rather than the alternate arrangement A' (inner methyl groups). The spectra of complexes 7 and 8 exhibit a pseudotriplet centered at 1.92 and 1.83 ppm, respectively, arising from the *trans*-PMe₂Ph ligands, and in the case of 8 a singlet at 3.70 ppm, attributed to the methyl proton resonance of the equivalent hydrazido ligands, indicating that a single isomer is present. The spectra of complexes 4 and 11 show a singlet at the same position, which is in agreement with the transformation of 4 into 11 (see below). The spectra of complexes 9 and 10 exhibit in the 3.60-2.15ppm range an asymmetrical multiplet due to the nonequivalent methylene groups of the coordinated dppe ligand. In addition, that of 10 shows also a singlet at 3.54 ppm corresponding to the methyl proton resonance of the hydrazido ligands and a weak singlet at 4.14 ppm attributed to a minor isomer (see below). In addition, the ¹H NMR spectra of all complexes show a complex multiplet in the 7.94-6.60 ppm range, corresponding to the phenyl proton resonances of the hydrazido(2-) and phosphine ligands.

As expected, the ${}^{31}P{}^{1}H$ NMR spectra of 3 and 11 exhibit a singlet at 36.98 and 38.05 ppm, respectively. The spectra of complexes 7 and 8 also show a single resonance at 1.24 and 1.44 ppm, respectively, indicating the equivalence of the *trans*phosphine ligands. However, the behavior of complexes 4-6is less simple. The spectrum of 4 exhibits two signals with equal intensities at 38.02 and -6.19 ppm; the latter can be unambiguously assigned to free triphenylphosphine, which indicates that 4 undergoes complete dissociation to give 11 and

Table 5. Selected Bond Lengths (Å) and Angles (deg) for $[Mo(NNMePh)_2Cl_2(PPh_3)_2]$ -0.5CH₂Cl₂

Mo(1) - Cl(1)	2.532(5)	Mo(51) - Cl(51)	2.500(5)
Mo(1) - Cl(2)	2.519(4)	Mo(51) - Cl(52)	2.529(5)
Mo(1) - P(1)	2.575(5)	Mo(51)-P(51)	2.570(5)
Mo(1) - P(2)	2.568(5)	Mo(51) - P(52)	2.570(5)
Mo(1) - N(1)	1.78(1)	Mo(51) - N(51)	1.80(1)
Mo(1) - N(11)	1.81(1)	Mo(51)-N(61)	1.83(1)
P(1)-C(15)	1.84(1)	P(51)-C(65)	1.84(1)
P(1) - C(21)	1.844(9)	P(51) - C(71)	1.813(9)
P(1) - C(27)	1.83(1)	P(51) - C(77)	1.858(9)
P(2) - C(33)	1.83(1)	P(52) - C(83)	1.83(1)
P(2) - C(39)	1.848(9)	P(52) - C(89)	1.83(1)
P(2) - C(45)	1.83(1)	P(52) - C(95)	1.85(1)
N(1) - N(2)	1.30(2)	N(51)-N(52)	1.31(2)
N(2) - C(1)	1.43(2)	N(52) - C(51)	1.42(2)
N(2) - C(7)	1.50(2)	N(52)-C(57)	1.48(2)
N(11) - N(12)	1.30(2)	N(61) - N(62)	1.30(2)
N(12) - C(8)	1.44(2)	N(62) - C(58)	1.43(2)
N(12) - C(14)	1.48(2)	N(62) - C(64)	1.50(2)
Cl(2)-Mo(1)-Cl(1)	80.7(1)	Cl(52) - Mo(51) - Cl(51)	80.3(2)
P(1) - Mo(1) - Cl(1)	94.2(2)	P(51) - Mo(51) - Cl(51)	83.5(2)
P(1) - Mo(1) - Cl(2)	84.6(1)	P(51) - Mo(51) - Cl(52)	96.9(2)
P(2) - Mo(1) - Cl(1)	84.0(2)	P(52) - Mo(51) - Cl(51)	92.5(2)
P(2) - Mo(1) - Cl(2)	91.1(1)	P(52) - Mo(51) - Cl(52)	83.6(2)
P(2) - Mo(1) - P(1)	175.6(2)	P(52) - Mo(51) - P(51)	175.8(2)
N(1) - Mo(1) - Cl(1)	168.0(4)	N(51) - Mo(51) - Cl(51)	165.7(4)
N(1) - Mo(1) - Cl(2)	89.3(4)	N(51) - Mo(51) - Cl(52)	87.5(4)
N(1) - Mo(1) - P(1)	91.5(4)	N(51) - Mo(51) - P(51)	90.6(4)
N(1) - Mo(1) - P(2)	89.5(4)	N(51) - Mo(51) - P(52)	93.6(4)
N(11)-Mo(1)-Cl(1)	88.7(4)	N(61) - Mo(51) - Cl(51)	89.8(4)
N(11) - Mo(1) - Cl(2)	167.5(4)	N(61) - Mo(51) - Cl(52)	167.9(4)
N(11) - Mo(1) - P(1)	89.7(4)	N(61) - Mo(51) - P(51)	89.0(4)
N(11) - Mo(1) - P(2)	94.3(4)	N(61) - Mo(51) - P(52)	89.8(4)
N(11) - Mo(1) - N(1)	102.0(6)	N(61) - Mo(51) - N(51)	103.1(6)
N(2)-N(1)-Mo(1)	170.2(11)	N(52)-N(51)-Mo(51)	159.4(11)
C(1) - N(2) - N(1)	119.4(13)	C(51) - N(52) - N(51)	118.5(12)
C(7) - N(2) - N(1)	119.9(15)	C(57) - N(52) - N(51)	120.6(13)
C(7) - N(2) - C(1)	120.7(14)	C(57) - N(52) - C(51)	120.6(13)
N(12)-N(11)-Mo(1)	163.9(11)	N(62) - N(61) - Mo(51)	164.7(12)
C(8) = N(12) = N(11)	118.4(13)	C(58) - N(62) - N(61)	116.9(13)
C(14) - N(12) - N(11)	120.4(14)	C(64) - N(62) - N(61)	120.6(14)
C(14) - N(12) - C(8)	121.1(13)	C(64) - N(62) - C(58)	122.4(13)
	- ()		

PPh₃. The spectrum of complex 5 shows three singlets in different intensities, indicating partial dissociation (ca. 12%) in CDCl₃; the more intense singlet at 13.05 ppm corresponds to the nondissociated species 5, while the other two, with equal intensities, at 25.89 and -27.60 ppm are assigned to a fivecoordinated complex similar to 3 and 11 and to free $PMePh_2$, respectively. This is in agreement with the ¹H NMR data (see above). The spectrum of complex 6 two singlets at 14.17 and 13.92 ppm in 1:2.8 ratio, which are assigned to isomers. Finally, the spectra of 9 and 10 display two doublets centered at 38.35 and 3.60 ppm with ${}^{2}J_{P-P} = 28.0$ Hz for the former and 42.62 and 9.35 ppm with ${}^{2}J_{P-P} = 35.0$ Hz for the latter, indicating unsymmetrical coordination of the dppe ligand.³⁷ Additionally, complex 10 shows two supplementary doublets of low intensity at 37.78 and 1.06 ppm, ${}^{2}J_{P-P} = 19.8$ Hz, attributed to a minor isomer.

Electrochemical Studies. Cyclic voltammetry (CV) studies of complexes 3–11 were carried out in CH₂Cl₂ at a platinum electrode at scan rates varying from 10 to 300 mV s⁻¹. The CV data are summarized in Table 6. The number of electrons transferred in the various steps was estimated to be 1 by comparison to the ferrocene oxidation under the same experimental conditions. The five-coordinated complexes 3 and 11 show an oxidation peak at +1.09 and +1.01 V, respectively, associated with a weak reduction peak at *ca.* +0.5 and +0.1 V, respectively. On the other hand, they display a reduction peak at -1.80 and -1.51 V, respectively, associated with a weak oxidation peak at *ca.* -0.2 V. This indicates that both oxidation and reduction processes are irreversible, the oxidized species,



Figure 1. View of the molecular structure of one of the independent molecules of $[Mo(NNPh_2)Cl_2(PPh_3)]$ in 3, with the atom-labeling scheme. (Chemically equivalent atoms in the independent molecules are labeled X_n and X_{50+n} , respectively.)



Figure 2. View of the molecular structure of one of the independent molecules of $[Mo(NNMePh)Cl_2(PPh_3)_2]$ in 40.5CH₂Cl₂, with the atomlabeling scheme. (Chemically equivalent atoms in the independent molecules are labeled X_n and X_{50+n}, respectively.)

[Mo(NNRPh)₂(PPh₃)Cl₂]⁺, and the reduced species, [Mo-(NNRPh)₂(PPh₃)Cl₂]⁻, being unstable in solution. The electrochemical behavior of **4** is more complicated due to the presence of **11** and free PPh₃ in solution. The six-coordinated complexes **5–8** exhibit a nearly-reversible one-electron oxidation process at *ca.* +0.87 V ($\Delta E_p = 120 \text{ mV}$ at 100 mV s⁻¹) and an irreversible one-electron reduction process in the -1.42 to -1.72 V range. Finally, the oxidation and reduction processes of complexes **9** and **10** are also irreversible; however, the dppe ligand shifts the oxidation and the reduction potentials to more positive and more negative values, respectively. In the broad lines, the electrochemical behavior of complexes 3 and 5-11 is similar to that of [organohydrazido(2-)]molyb-denum complexes containing dithiocarbamate³⁸ and acetylacetonate¹³ ancillary ligands.

Conclusion. Mixed [organohydrazido(1-)][organohydrazido-(2-)]molybdenum complexes [(MoNHNRPh)(NNRPh)(acac)-

⁽³⁸⁾ Crichton, B. A. L.; Dilworth, J. R.; Pickett, C. J.; Chatt, J. J. Chem. Soc., Dalton Trans. 1981, 419.



Table 6. Cyclic Voltammetric Data (V νs SCE) in CH_2Cl_2 Solution

	$E_{\mathrm{p}},$	V
complex	redn	oxidn
3	-1.80	1.09
5	-1.42	0.93
6	-1.62	0.86
7	-1.44	0.83
8	-1.72	0.86
9	-1.71	1.37
10	-1.77	1.31
11	-1 51	1.01

 Cl_2] (R = Me, Ph) have proved to be suitable precursors in the synthesis of a number of five- and six-coordinated bis-[organohydrazido(2-)]molybdenum complexes containing ancillary tertiary phosphine ligands. The product stoichiometry appears to be dictated mainly by steric effects. The fivecoordinated complexes and the most strained six-coordinated complex react with acetylacetone, giving back the precursors. These results demonstrate the reversible behavior of the [Mo-(NHNRPh)(NNRPh)]³⁺/[Mo(NNRPh)₂]²⁺ couple.

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Supplementary Material Available: Tables giving crystal data, anisotropic thermal parameters, and bond lengths and bond angles for compounds 3 and 40.5CH₂Cl₂ (7 pages). Ordering information is given on any current masthead page.