Insight into Formation and Reactivity of Molybdenum(0) Bent Nitrenes. Crystal Structure of a Phosphine–Phosphoranimine Chelate

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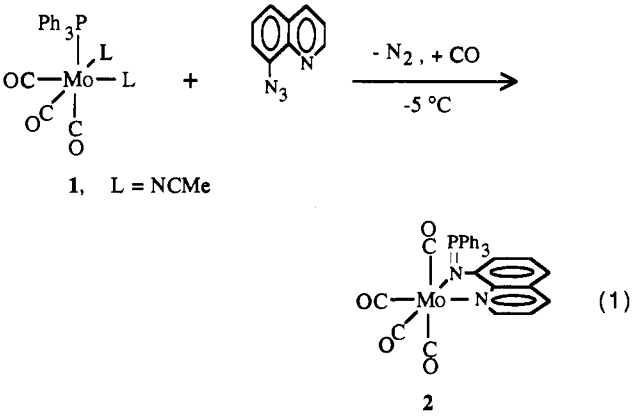
Introduction

Transition metal nitrene (imido) complexes are typically composed of high-valent metals with linear M–N–R geometries and formal M–N triple bonds.[1] Bent nitrenes, with formal M–N double bonds, are more rare and are expected to be more reactive than linear nitrenes.[2] Indeed, it has recently been demonstrated that the transient bent-nitrene molybdenum(0) and tungsten(0) complexes [$(CO)_3(Ph_3P)Mo{=}NR$] (R = quinoline)[3] and [$(CO)_5W{=}NR$] (R = Ph)[4] react rapidly with phosphines to form phosphoranimine complexes {$M(R'_3P{=}NR)$}.

Our strategy for preparing a bent nitrene is to constrain the geometry at nitrogen by incorporating the nitrene into a chelate ring. We chose 8-azidoquinoline (8-AZQ) as the nitrene precursor because organic azides have been used to prepare high-oxidation-state nitrene complexes[1,2c] and coordination of a quinoline–nitrene ligand in a bidentate fashion would produce a five-membered chelate ring incorporating a bent M=N—R unit. We have recently reported the synthesis and X-ray structure of the molybdenum(0) phosphoranimine complex [$(CO)_4Mo(Ph_3P{=}NR)$] (R = quinoline) (**2**), which is prepared by reaction of [$Mo(CO)_3(PPh_3)(CH_3CN)_2$] (**1**) and 8-AZQ in the presence of CO (eq 1).[3] The following points are consistent with the intermediacy of a molybdenum(0) bent-nitrene complex in this reaction: (1) 8-AZQ reacts with **1** via loss of dinitrogen, (2) formation of the phosphoranimine ligand is metal-mediated, (3) the reaction is first order in azide and first order in **1**, and (4) 8-AZQ reacts with [*fac*-$Mo(CO)_3(CH_3CN)_3$] (**3**) in the absence of phosphine, to form the neutral, 8-aminoquinoline complex [$(CO)_3(CH_3CN)Mo\{N(H)_2C_9H_6N\}$].[3]



During the course of investigation of the reaction shown in eq 1, several questions arose: (1) what is the role of the quinoline nitrogen, i.e., will nonchelating azides react via loss of dinitrogen to form molybdenum(0) nitrenes, (2) how many vacant coordination sites at molybdenum are required for reactivity with 8-AZQ, and (3) does phosphoranimine formation occur via intra- or intermolecular reaction of phosphine with a bent-nitrene molybdenum complex? We now report experiments that address these points as well as the crystal structure of a phosphine–phosphoranimine chelate, [$(CO)_3Mo\{(Ph)_2PCH_2(Ph)_2P{=}NC_9H_6N\}$].

Experimental Section

General Considerations. All manipulations were carried out under an atmosphere of nitrogen which was purified by passage through a column of Linde 4A molecular sieves and activated Chemical Dynamics Corp. R3-11 catalyst. Solutions were handled using standard Schlenk methods, and solids were transferred in a Vacuum Atmospheres Corp. glovebox.[5] Acetonitrile was purchased from J. T. Baker or Aldrich, distilled from CaH_2 under nitrogen, and used immediately. Deuterium-labeled NMR solvents were purchased from Cambridge Isotope Laboratory. Phosphines were purchased from Strem or Aldrich and were used without further purification. 8-Aminoquinoline, 5-aminoquinoline, and 2-aminonaphthalene were purchased from Aldrich.

Proton and ^{31}P NMR spectra were recorded in CD_2Cl_2 on a Varian XL-200 FT-NMR instrument, operating at 200 and 81 MHz, respectively. Phosphorus spectra were referenced vs 85% H_3PO_4. Infrared spectra were obtained on a Midac FT-IR spectrophotometer (Model 101025). FAB mass spectra were obtained on a JEOL SX-102 mass spectrometer operating in the positive-ion mode, and the sample was suspended in *m*-nitrobenzyl alcohol.

Syntheses. The organic azides, 8-azidoquinoline, 2-azidonaphthalene, and 5-azidoquinoline were prepared from the corresponding amines according to the published general procedure A reported by Smith and Brown[6] with modifications as follows: 8-azidoquinoline and 5-azidoquinoline were precipitated from the reaction mixture by addition of 10% aqueous Na_2CO_3, and 2-aminonaphthalene was dissolved in H_2SO_4. IR (CH_3CN, cm^{-1}): $\nu(N{=}N{=}N)$ 2118 (8-azidoquinoline), 2116 (2-azidonaphthalene), 2122 (5-azidoquinoline).

The phosphoranimines $(Ph)_2PCH_2P(Ph)_2{=}NR$ ($R = C_9H_6N, C_{10}H_7$) were prepared in CH_3CN at room temperature by reaction of 1 equivalent of dppm and 8-AZQ or 2-azidonaphthalene, respectively. $(Ph)_2PCH_2P(Ph)_2{=}NC_9H_6N$: ^1H NMR δ 8.1 (dd, 1H, quinoline), 7.8–6.9 (m, 25H, quinoline + phenyl), 3.68 (d, $J(H,P^{III}) = 1.2$ Hz, $J(H,P^{V}) = 11.9$ Hz, 2H, CH_2). $^{31}P\{^1H\}$NMR δ 3.5 (d, P^V, $J(P,P) = 52$ Hz), −28.0 (d, P^{III}, $J(P,P) = 52$ Hz); IR (Nujol, cm^{-1}) 1329 (s), 1232 (w), 1182 (s), 1126 (s), 1109 (s), 1026 (m), 982 (s), 862 (m), 820 (s), 788 (w), 733 (s), 692 (s). $(Ph)_2PCH_2P(Ph)_2{=}NC_{10}H_7$: ^1H NMR δ 7.85–6.65 (m, 27H, naphthalene + phenyl), 3.31 (d, $J(H,P) = 12.6$ Hz, 2H, CH_2).

[*fac*-$Mo(CO)_3(CH_3CN)_3$] (**3**) was prepared in situ by photolysis of $Mo(CO)_6$ in CH_3CN solution using a 200- or 350-W Oriel high-pressure mercury arc lamp with Pyrex-filtered light.[7] [$Mo(CO)_3(LL)(L_1)$] (**4a–d**) (LL = dppm, $L_1 = CH_3CN$, **4a**; LL = dppe, $L_1 = CH_3CN$, **4b**; LL = dppe, $L_1 = CH_3C(O)CH_3$, **4c**; LL = dmpe, $L_1 = CH_3CN$, **4d**): All complexes except **4c** were prepared by addition of 1 molar equiv of the appropriate bis(phosphine) ligand to an CH_3CN solution of **3**. Complex **4c** was prepared by photolysis of $Mo(CO)_4(dppe)$ in acetone.[8] IR $\nu(CO)$: **4a** (CH_3CN, cm^{-1}) 1933, 1834, 1819; **4b** (CH_3CN, cm^{-1}) 1931, 1836, 1817; **4c** ($CH_3C(O)CH_3$, cm^{-1}) 1927, 1831, 1805; **4d** (CH_3CN, cm^{-1}) 1923, 1825, 1800. ^1H NMR, **4a**: δ 7.8–7.2 (m, 20H, phenyl), 4.8 (dt, $J(H,H) = 15.3$ Hz, $J(H,P) = 7.8$ Hz, 1H, CH_2), 4.0 (dt, $J(H,H) = 15.3$ Hz, $J(H,P) = 9.5$ Hz, 1H, CH_2), 1.35 (t, $J(H,P) = 1.5$ Hz, CH_3CN).

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Table I. Crystallographic Data for $[Mo(CO)_3\{(Ph)_2PCH_2P(Ph)_2{=}NC_9H_6N\}]$ (**5a**)

chem formula	$C_{37}H_{28}MoN_2O_3P_2$
fw	706.5
color; habit	dark red needles
cryst size	0.20 × 0.50 × 0.52 mm^3
cryst system	monoclinic
space group	$P2_1/c$ (No. 14)
unit cell dimens	a = 20.627(3) Å b = 19.769(3) Å c = 16.948(2) Å β = 111.40(1)°
vol	6434(1) Å^3
Z	8
λ	0.710 73 Å
density (calc)	1.459 g/cm^3
abs coeff	0.533 mm^{-1}
temp	230 K
transm coeff: max, min	0.9063, 0.7830
R^a	4.98%
$R_w{}^a$	4.45%

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

$[Mo(CO)_2(dppe)(CH_3CN)_2]$ (**4e**) was prepared by photolysis of $[Mo(CO)_3(dppe)(CH_3CN)]$ (**4b**) in CH_3CN solution. IR (CH_3CN, cm^{-1}): ν(CO) 1825, 1753 cm^{-1}.

Tricarbonyl{8-[((diphenylphosphino-κP)methyl)diphenylphosphoranimyl-κN]quinoline-κN}molybdenum(0), $[Mo(CO)_3\{(Ph)_2PCH_2P(Ph)_2{=}NC_9H_6N\}]$ (**5a**). Addition of 0.4 mmol of **4a** in 25 mL of CH_3CN solution to 68 mg of crystalline 8-azidoquinoline (0.4 mmol) produces an orange-red solution. After 2–3 h of stirring at room temperature, red microcrystalline **5a** was collected by filtration (115 mg, 40%). Complex **5a** forms in 65% yield (by ^{1}H NMR), but the isolated yield is typically 35–40%. Complex **5a** was also prepared by reaction of **3** and $(Ph)_2PCH_2P(Ph)_2{=}NC_9H_6N$. ^{1}H NMR: δ 9.34 (dt, 1H, quinoline), 8.04 (m, 1H, quinoline), 7.97–7.01 (m, 20 H, phenyl), 6.81–6.67 (m, 3H, quinoline), 5.91 (m, 1H, quinoline), 3.97 (m, J(H,H) = 14.8 Hz, $J(H,P_A)$ = 3.1 Hz, $J(H,P_B)$ = 7.0 Hz, 1 H, CH_2), 3.58 (m, J(H,H) = 14.8, $J(H,P_A)$ = 5.4 Hz, $J(H,P_B)$ = 14.8 Hz, 1H, CH_2). IR (Nujol, cm^{-1}): 1908 (vs), 1802 (vs), 1776 (vs); 1566 (m), 1321 (s), 1281 (m), 1190 (w), 1126 (s), 1115 (s), 1024 (w), 976 (m), 862 (w), 823 (w), 742 (s), 692 (s). FAB-MS, m/z: 678, $(M - CO)^+$; 527, $(M - 3CO - Mo + H)^+$.

Complex **5a** is slightly air and moisture sensitive. At room temperature **5a** decomposes in CH_3CN solution in the presence of H_2O over several days to form free 8-aminoquinoline and phosphine oxides $\{(Ph)_2PCH_2P(O)(Ph)_2$ and $(Ph)_2P(O)CH_2P(O)(Ph)_2\}$. 8-Aminoquinoline was identified by comparison of its ^{1}H NMR spectrum to that of an authentic sample; $(Ph)_2PCH_2P(O)(Ph)_2$ and $(Ph)_2P(O)CH_2P(O)(Ph)_2$ were identified by comparison of ^{1}H NMR data to literature values.[9] The molybdenum product has not been completely characterized, but it appears to contain carbonyl and oxo ligands. IR (Nujol, cm^{-1}): ν(CO) 1924, 1834; ν(Mo=O) 904. Free phosphoranimine $(Ph)_2PCH_2P(Ph)_2{=}NR$ (R = quinoline) also reacts slowly with H_2O to form 8-aminoquinoline and the partially oxidized phosphine $(Ph)_2PCH_2P(O)(Ph)_2$. Thus, it seems likely that dissociation of the phosphoranimine ligand from **5a** occurs prior to oxidation.

Reaction Studies. Reactions of aryl azides and molybdenum(0) carbonyl complexes (generated in situ as described above) were carried out at room temperature on dilute solutions (typically ≤10 mM) containing equal molar ratios of azide and molybdenum. Reactions were monitored by using IR spectroscopy, following changes in the carbonyl region and in the ν(N=N=N) stretch near 2120 cm^{-1}. Under these conditions, reaction of **4a** and 8-AZQ to form **5a** is complete in 1 h. In contrast, in the reaction of **4a** and 2-azidonaphthalene, there is only a 10% decrease in the ν(N=N=N) band in 1 h. Assignment of the product as a (phosphine–phosphoranimine)molybdenum complex is based on a comparison of ^{1}H NMR data in the methylene region to those of the free phosphoranimine. ^{1}H NMR: δ 3.57 (dd, $J(H,P_A)$ = 10.6 Hz, $J(H,P_B)$ = 9.6 Hz, 2H, CH_2).

Kinetic Studies. The rate of disappearance of the ν(N=N=N) band at 2118 cm^{-1} was measured at room temperature in CH_3CN as a function of concentration of **4a** and 8-AZQ: [**4a**] = 4.5–9.1 mM; [8-AZQ] = 4.5–9.1 mM.

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for Non-Hydrogen Atoms in Molecule A of Complex **5a**

atom	x	y	z	U(eq)
Mo	4781(1)	1016(1)	1634(1)	25(1)
P(1)	4455(1)	823(3)	3369(1)	28(1)
P(2)	5027(1)	−115(1)	2380(1)	29(1)
O(1)	4517(2)	2520(2)	1015(3)	56(2)
O(2)	6151(2)	1579(2)	2953(2)	48(2)
O(3)	5639(2)	720(2)	496(3)	57(2)
N(1)	3689(2)	796(2)	727(2)	30(2)
N(2)	4073(2)	1022(2)	2394(2)	28(1)
C(1)	4600(2)	1961(3)	1228(3)	33(2)
C(2)	5633(3)	1351(3)	2458(3)	32(2)
C(3)	5306(3)	836(3)	910(3)	36(2)
C(4)	3500(3)	654(3)	−93(3)	40(2)
C(5)	2812(3)	662(3)	−657(3)	48(2)
C(6)	2294(3)	814(3)	−382(4)	49(2)
C(7)	2456(3)	971(3)	478(3)	38(2)
C(8)	1958(3)	1170(3)	821(4)	53(3)
C(9)	2154(3)	1343(3)	1647(4)	49(3)
C(10)	2861(3)	1304(3)	2206(3)	40(2)
C(11)	3368(2)	1095(2)	1906(3)	32(2)
C(12)	3173(2)	950(2)	1028(3)	29(2)
C(13)	5078(2)	150(3)	3453(3)	31(2)
C(14)	5863(2)	−557(3)	2640(3)	30(2)
C(15)	5942(3)	−1248(3)	2730(3)	45(2)
C(16)	6599(3)	−1544(3)	2951(4)	56(3)
C(17)	7171(3)	−1150(3)	3069(4)	51(3)
C(18)	7101(3)	−470(3)	2989(4)	60(3)
C(19)	6448(3)	−170(3)	2758(4)	51(3)
C(20)	4388(3)	−798(2)	2118(3)	30(2)
C(21)	3951(3)	−860(3)	1277(3)	36(2)
C(22)	3462(3)	−1381(3)	1021(4)	46(2)
C(23)	3424(3)	−1847(3)	1602(4)	48(3)
C(24)	3860(3)	−1807(3)	2434(4)	48(3)
C(25)	4339(3)	−1276(3)	2689(3)	42(2)
C(26)	4941(2)	1517(3)	4000(3)	32(2)
C(27)	5496(3)	1402(3)	4750(3)	38(2)
C(28)	5848(3)	1944(3)	5231(3)	50(3)
C(29)	5641(3)	2588(3)	4970(4)	52(3)
C(30)	5096(3)	2708(3)	4231(4)	57(3)
C(31)	4732(3)	2171(3)	3733(3)	44(2)
C(32)	3871(3)	525(3)	3874(3)	32(2)
C(33)	3806(3)	845(3)	4566(3)	42(2)
C(34)	3341(3)	609(3)	4923(4)	55(3)
C(35)	2950(3)	48(3)	4588(4)	59(3)
C(36)	3004(3)	−272(3)	3892(4)	55(3)
C(37)	3460(3)	−43(3)	3533(3)	41(2)

Crystal Structure of $[Mo(CO)_3\{(Ph)_2PCH_2P(Ph)_2{=}NC_9H_6N\}]$ (5a). Crystals of **5a** were obtained by cooling the reaction mixture for 24 h. A dark red needle was cut to 0.20 × 0.50 × 0.52 mm^3, mounted on a glass fiber with epoxy cement, and then transferred to a Siemens R3m four-circle diffractometer for characterization and data collection at 230 K. Unit cell parameters for the sample were determined from the angular settings of 25 well-centered reflections ($25 \le 2\theta \le 30°$). Crystallographic data are summarized in Table I.

One quadrant of data ($+h,+k,\pm l$) was collected in the ω scan mode with 2θ ranging from 4.0 to 50.0° and scan speeds varying from 4.0 to 29.3°/min. Three standards are measured for every 97 reflections during the data collection period and showed no deviations from their mean intensity values (0.9845, 1.0048, and 1.0368 for minimum, mean, and maximum respectively). A total of 12 009 reflections were measured, and corrected for Lorentz-polarization and absorption effects. No extinction was detected. Of these, 11 302 were unique and 7993 reflections had $F > 3.0\sigma(F)$ and were considered observed.

The structure was successfully solved by the heavy-atom methods (XS: PATT) in the monoclinic space group $P2_1/c$ (No. 14) and refined by full-matrix least-squares procedures.[10] All of the non-hydrogen atoms were refined with anisotropic temperature parameters, hydrogen atoms were allowed to ride on their respective carbons [C–H = 0.96 Å, U(H) = 1.2U(C)], and a weighting scheme based on $\sigma(F)$ was employed. During the refinements, the 810 positional and anisotropic displacement parameters were grouped into two blocks of 405 parameters each. The first block contained all of the parameters for one of the two independent molecules in the asymmetric unit, while the second block contained all of the parameters for the second independent molecule. The parameters

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Table III. Selected Bond Distances (Å) and Angles (deg) for Molecule A of **5a**

Bond Distances			
Mo–P(2)	2.528(1)	Mo–N(1)	2.259(3)
Mo–N(2)	2.273(4)	Mo–C(1)	1.978(5)
Mo–C(2)	1.919(4)	Mo–C(3)	1.942(6)
P(1)–N(2)	1.598(4)	P(1)–C(13)	1.820(5)
P(1)–C(26)	1.802(5)	P(1)–C(32)	1.813(6)
P(2)–C(13)	1.857(5)	P(2)–C(14)	1.838(5)
P(2)–C(20)	1.824(5)	O(1)–C(1)	1.156(7)
O(2)–C(2)	1.182(5)	O(3)–C(3)	1.171(8)
N(1)–C(4)	1.329(6)	N(1)–C(12)	1.371(7)
N(2)–C(11)	1.395(5)		
Bond Angles			
P(2)–Mo–N(1)	97.9(1)	P(2)–Mo–N(2)	76.9(1)
N(1)–Mo–N(2)	72.5(1)	P(2)–Mo–C(1)	170.7(2)
N(1)–Mo–C(1)	86.0(2)	N(2)–Mo–C(1)	96.5(2)
P(2)–Mo–C(2)	88.7(2)	N(1)–Mo–C(2)	169.2(2)
N(2)–Mo–C(2)	101.1(2)	C(1)–Mo–C(2)	86.2(2)
P(2)–Mo–C(3)	95.6(2)	N(1)–Mo–C(3)	100.5(2)
N(2)–Mo–C(3)	168.6(2)	C(1)–Mo–C(3)	91.9(2)
C(2)–Mo–C(3)	87.2(2)	N(2)–P(1)–C(13)	109.1(2)
N(2)–P(1)–C(26)	112.6(2)	C(13)–P(1)–C(26)	106.6(2)
N(2)–P(1)–C(32)	114.0(2)	C(13)–P(1)–C(32)	107.3(2)
C(26)–P(1)–C(32)	106.8(3)	Mo–P(2)–C(13)	99.8(2)
Mo–P(2)–C(14)	122.6(2)	C(13)–P(2)–C(14)	100.7(2)
Mo–P(2)–C(20)	122.6(1)	C(13)–P(2)–C(20)	103.1(2)
C(14)–P(2)–C(20)	103.7(2)	Mo–N(1)–C(4)	126.3(4)
Mo–N(1)–C(12)	114.9(3)	C(4)–N(1)–C(12)	117.7(4)
Mo–N(2)–P(1)	114.2(2)	Mo–N(2)–C(11)	114.3(3)
P(1)–N(2)–C(11)	130.7(4)	Mo–C(1)–O(1)	177.4(4)
Mo–C(2)–O(2)	177.7(4)	Mo–C(3)–O(3)	177.9(4)
N(1)–C(4)–C(5)	123.6(6)	P(1)–C(13)–P(2)	110.1(2)

in each of these blocks were varied in alternate least-squares cycles. Structural data for one independent molecule (molecule A) are provided in Table II (atomic coordinates and equivalent isotropic displacement coefficients) and Table III (selected bond lengths and angles). The corresponding data for the second independent molecule (molecule B) are available as supplementary material.

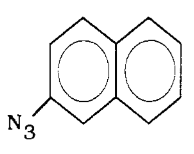
Results and Discussion

Chelation and Vacant Coordination Site Studies. The chelate effect is a useful phenomenon in ligand substitution reactions. For example, in the reaction of dppe and $Mo(CO)_5$ (generated by heating or irradiating $Mo(CO)_6$ in a weakly coordinating solvent), rapid displacement of a second carbon monoxide occurs following coordination of the first phosphorus atom of the chelating dppe.[11] Our strategy for using 8-AZQ in reactions with molybdenum(0) complexes is to make use of the chelate effect to prepare a bent nitrene. However, the bent-nitrene intermediate postulated to occur in the reaction shown in eq 1 has been too reactive to isolate or even spectroscopically detect.[3] Thus, we have shifted our emphasis toward understanding how modification of aryl azides may enhance the stability or control the reactivity of the resulting metal nitrene. As a first step toward this goal, we have undertaken experiments to determine the extent to which the quinoline nitrogen participates in the reaction of aryl azides with molybdenum(0) complexes and whether more than one vacant coordination site at molybdenum is required.

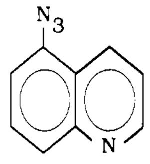
Reaction of 0.2 mmol of [*fac*-$Mo(CO)_3(CH_3CN)_3$] (**3**) and 1 molar equiv of 8-AZQ is complete within 5–10 min at room temperature, as indicated by the complete disappearance of the $\nu(N{=}N{=}N)$ stretch at 2118 cm^{-1}.[12] In contrast, there is no reaction between **3** (0.22 mmol) and 1 equiv of the nonchelating azide, 2-azidonaphthalene or 5-azidoquinoline, even after 7 h at room temperature. These observations demonstrate that reaction of the aryl azide is facilitated by coordination of a quinoline nitrogen which is positioned on the same side of the fused rings as the azide group such that a metallacycle is formed. These experiments also suggest that a requirement for reactivity of 8-AZQ with molybdenum(0) complexes is the presence of at least two cis open-coordination sites provided by weakly bound solvent molecules. Consistent with this notion, we find that 8-AZQ does not react with [*fac*-$Mo(CO)_3(PPh_3)_2(CH_3CN)$]. Thus chelation is important in reactions of 8-AZQ and molybdenum(0) complexes, but it does not result in displacement of a carbon monoxide or phosphine ligand.

Table IV. Chelate Reaction Data for Reaction of 8-AZQ and $Mo(CO)_2(LL)L_1L_2$

complex	LL	L_1	L_2	LL cone angle,[13] deg	phosphoranimine product?
4a	dppm	CH_3CN	CO	121	yes
4b	dppe	CH_3CN	CO	125	no
4c	dppe	$CH_3C(O)CH_3$	CO	125	no
4d	dmpe	CH_3CN	CO	107	no
4e	dppe	CH_3CN	CH_3CN	125	no

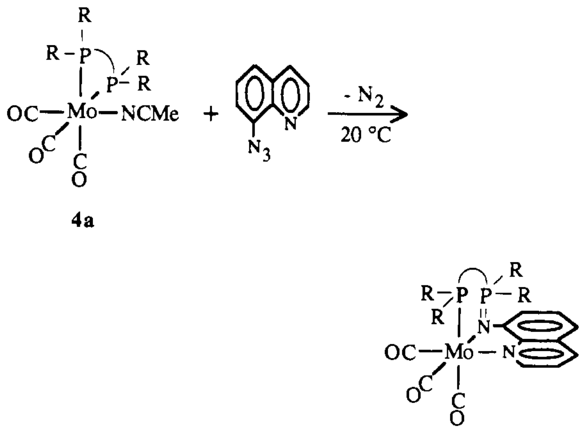


2 - azidonaphthalene



5 - azidoquinoline

Reaction of 8-AZQ and Molybdenum(0) Bis(phosphine) Complexes. Of the molybdenum(0) bis(phosphine) complexes shown in Table IV, only [$(CO)_3Mo(dppm)(CH_3CN)$] (**4a**) reacts with 8-AZQ to form a phosphine–phosphoranimine chelate in good yield (≈60%): [$(CO)_3Mo\{(Ph)_2PCH_2(Ph)_2P{=}NC_9H_6N\}$] (**5a**) (see eq 2). There is no reaction between 8-AZQ and **4b** possibly because the acetonitrile ligand in **4b** is strongly bound. However **4c**, which contains a more labile ligand,[8] also does not react with 8-AZQ, nor does the more electron-rich and sterically less-crowded complex **4d**. Interestingly, as expected on the basis of the requirement of two open-coordination sites at molybdenum (vide supra), there is a reaction between **4e** and 8-AZQ. However, the



4a

5a

(2)

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(10) SHELXTL PLUS 4.11 for *R3/V* and *R3m/V* crystallographic systems: G. M. Sheldrick, University of Goettingen, FRG, and Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1990. All computations were performed on a Micro VAX computer. Neutral-atom scattering factors were used as stored in the SHELXTL PLUS structure determination package, and all non-hydrogen scattering factors were corrected for both the real and imaginary components of anomalous dispersion.

(11) Connor, J. A.; Day, J. P.; Jones, E. M.; McEwen, G. K. *J. Chem. Soc., Dalton Trans.* **1973**, 347.

(12) The product of this reaction is an aminoquinoline complex; see ref 3.

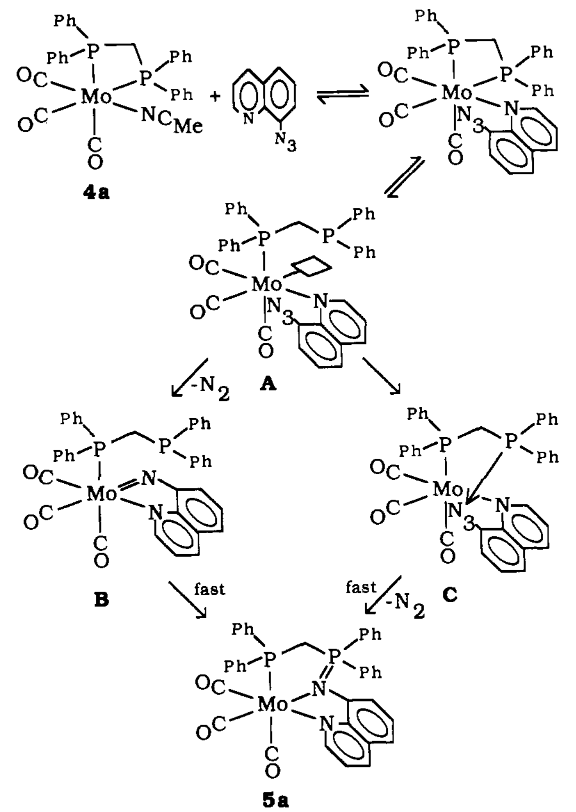
(13) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

primary quinoline-containing product is 8-aminoquinoline, not a phosphine–phosphoranimine complex. (A small amount (<10%) of free phosphoranimine $(Ph)_2PCH_2CH_2P(Ph)_2{=}NC_9H_6N$ forms, probably as a result of reaction of 8-AZQ and free dppe generated by decomposition of **4e**). For comparison, in the reaction of **4a** and 8-AZQ, 8-aminoquinoline does not form. The formation of 8-aminoquinoline in the reaction of **4e** and 8-AZQ is noteworthy since in other reactions of 8-AZQ with molybdenum(0) carbonyl complexes, aminoquinoline products form only when there is no phosphine or a more electron-withdrawing phosphine [e.g., $P(OR)_3$] is present in the molybdenum coordination sphere.[3]

We hypothesize that a key mechanistic requirement for reactivity of 8-AZQ and the bis(phosphine) complexes **4a–d** is dissociation of one arm of the chelating phosphine to create a second open coordination site. Since dppm forms a strained four-membered chelate ring, compared to the relatively stable five-membered chelates in **4b–d**, we propose that, in CH_3CN solution, there is an equilibrium between an η^2-dppm (**4a**) and an η^1-dppm complex.[14] The room-temperature ^1H NMR spectrum of **4a** reveals two sharp multiplets for inequivalent methylene protons in chelated dppm. This suggests that if the chelate ring opens, the equilibrium concentration of the η^1-dppm complex is too low to detect by NMR. However, the following observations are consistent with an η^2-dppm $\leftrightarrow$ η^1-dppm equilibrium for **4a**. First, complex **4a** slowly decomposes in CD_2Cl_2 to form $Mo(CO)_3(\eta^2\text{-dppm})(\eta^1\text{-dppm})$[14d] as one of the decomposition products. In substitution reactions of metal(0) carbonyl bis(phosphine) complexes in which the bidentate phosphine ligand is lost, a mechanism involving ring opening of the chelate is favored.[15] Second, **4a** reacts very slowly with 2-azidonaphthalene, forming a phosphine–phosphoranimine complex (see Experimental Section). In contrast, free dppm reacts rapidly with 2-azidonaphthalene to form free phosphoranimine $(Ph)_2PCH_2P(Ph)_2{=}N(C_{10}H_7)$. The slower rate of reaction of **4a** and 2-azidonaphthalene is clearly a consequence of coordination of dppm to molybdenum. Furthermore, 2-azidonaphthalene does not react with $Mo(CO)_3(CH_3CN)_3$ because there is no quinoline nitrogen to facilitate reaction of the azide (vide supra). Thus, in the reaction of 2-azidonaphthalene and **4a**, the azide does not react at a vacant coordination site but rather reacts directly with one of the dangling arms of dppm. Finally, complex **4b**, which has a chelating dppe ligand, does not react with 2-azidonaphthalene. While chelating ring opening may also be occurring in the dppe complexes, the equilibrium concentration of the ring-opened complex must be even lower than in **4a**, again consistent with the reactions summarized in Table IV.

The results of preliminary kinetic experiments involving eq 2 are consistent with a rate law first order in **4a** and 8-AZQ. In addition, reaction 2 is 10 times slower than reaction 1, which is also first order in both molybdenum and azide.[3] This is consistent with a mechanism that incorporates an η^2-dppm $\leftrightarrow$ η^1-dppm equilibrium prior to or in the rate-determining step (rds).[16] If dissociation of phosphine is rate limiting, then coordination of quinoline prior to dissociation of phosphine is consistent with the rate law. A possible sequence of events for reaction of **4a** and 8-AZQ is summarized in Scheme I. The intermediate A is expected to react quickly by formation of a bent nitrene (**B**) or react in a concerted reaction, **C** $\Rightarrow$ **5a**. The concerted pathway involves formation of an enthalpically unfavorable eight-membered ring, while formation of nitrene intermediate **B** yields a more favorable five-membered ring. The intermediacy of a bent nitrene is also supported by the chemistry observed for other low-valent metal nitrenes.[3,4] For example, the tungsten(0) nitrene complex $(CO)_5W(NPh)$ is trapped by external (free) PPh_3 to form $(CO)_5W(Ph_3P{=}NPh)$.[4]

Scheme I



X-ray Structure and Spectroscopic Data for $[(CO)_3Mo\{(Ph)_2PCH_2(Ph)_2P{=}NC_9H_6N\}]$ (5a). Interest in P–N multiple bonding and reactivity has stimulated investigations of the synthetic utility of phosphoranimines ($R_3P{=}NR'$).[17] However, there are few examples of their use as ligands for transition metals and structurally characterized phosphoranimine complexes are rare.[3,18] The crystal structure of **5a** was obtained, and a view of the molecule is shown in Figure 1. The structure reveals a facial tricarbonylmolybdenum(0) complex with a distorted octahedral coordination geometry. The molybdenum atom is slightly below and the imine phosphorus (P(1)) is slightly above the plane defined by the 10-atom heterocyclic quinoline ring (Mo and P atoms in each independent molecule are out of plane by <0.85 Å). The phosphoranimine N(2) is shared by two five-membered chelate rings. The average P–N bond distance of 1.595(4) Å in the two independent molecules of **5a** is very similar to the values observed in several closely related phosphoranimine complexes and is indicative of π interaction between P and N.[3,18] The angles around N(2) average 120°, consistent with trigonal planar geometry.

Infrared spectral data are also consistent with a significant degree of multiple bonding in the P–N bond. Comparison of

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(14) Metal carbonyl complexes with η^1-dppm ligands are well-known. For examples, see: (a) Cano, M.; Campo, J. A.; Perez-Garcia, V.; Gutierrez-Puebla, E.; Alvarez-Ibarra, C. *J. Organomet. Chem.* **1990**, *382*, 397. (b) Blagg, A.; Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1987**, 1495. (c) Hor, T. S. A.; Che, S.-M. *J. Organomet. Chem.* **1987**, *331*, 23. (d) Isaacs, E. E.; Graham, W. A. G. *Inorg. Chem.* **1975**, *14*, 2568.

(15) (a) Halverson, D. E.; Reisner, G. M.; Dobson, G. R.; Bernal, I.; Mulcahy, T. L. *Inorg. Chem.* **1982**, *21*, 4285. (b) Macholdt, H.-T.; van Eldik, R.; Dobson, G. R. *Inorg. Chem.* **1986**, *25*, 1914.

(16) Rosseinsky, D. R. *J. Chem. Soc., Dalton Trans.* **1979**, 731.

(17) For recent examples, see: (a) Molina, P.; Alajarín, M.; López-Lázaro, A. *Tetrahedron* **1991**, *47*, 6747. (b) Molina, P.; Vilaplana, M. J.; Pérez, J. *Ibid.* **1990**, *46*, 7855.

(18) (a) Imhoff, P.; Nefkens, S. C. A.; Elsevier, C. J.; Goubitz, K.; Stam, C. H. *Organometallics* **1991**, *10*, 1421. (b) Vicente, J.; Chicote, M.-T.; Fernández-Baeza, J.; Lahoz, F. J.; López, J. A. *Inorg. Chem.* **1991**, *30*, 3617. (c) Katti, K. V.; Batchelor, R. J.; Einstein, F. W. B.; Cavell, R. G. *Ibid.* **1990**, *29*, 808. (d) Katti, K. V.; Cavell, R. G. *Ibid.* **1989**, *28*, 413. (e) Katti, K. V.; Cavell, R. G.; *Organometallics* **1989**, *8*, 2147. (f) Cramer, R. E.; Roth, S.; Gilje, J. W. *Ibid.* **1989**, *8*, 2327. (g) Maurer, A.; Fenske, D.; Beck, J.; Hiller, W.; Strähle, J.; Böhm, E.; Dehnicke, K. *Z. Naturforsch., B.* **1988**, *43*, 5. (h) Miller, J. S.; Visscher, M. O.; Caulton, K. G. *Inorg. Chem.* **1974**, *13*, 1632.

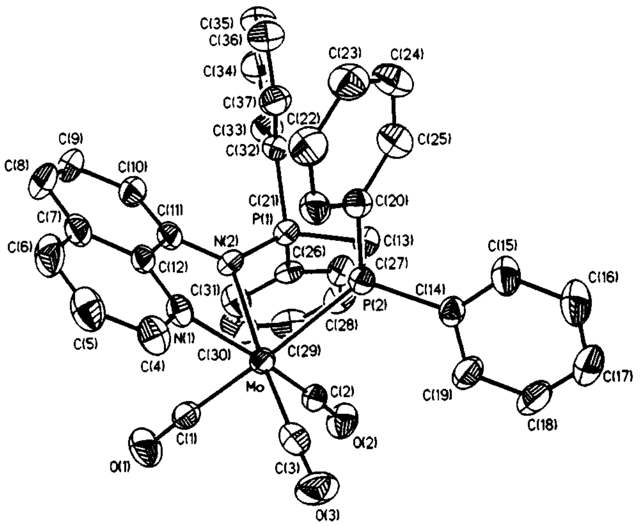

Figure 1. Thermal ellipsoid plot of molecule A of **5a** at the 50% probability level.

solid-state IR spectra for **5a** and the corresponding free phosphoranimine, $(Ph)_2PCH_2P(Ph)_2{=}N(C_9H_6N)$, reveals that the band at 1329 cm^{-1} for the free ligand [assigned as ν(P–N)][19] splits into two weaker bands that are shifted slightly to lower energy (1321, 1281 cm^{-1}) for **5a**. For comparison, the P–N stretch at 1327 cm^{-1} for the free phosphoranimine $Ph_3P{=}N(C_9H_6N)$ shifts to 1306 and 1265 cm^{-1} for $[(CO)_4Mo(Ph_3P{=}NC_9H_6N)]$ (**2**), which has a P–N bond distance of 1.626 Å.[3] NMR data reveal that the structure of **5a** is maintained in solution; the CH_2 protons in the phosphine chelate ring are inequivalent, and each couples to two inequivalent P atoms, giving rise to two sets of multiplets centered at 3.97 and 3.58 ppm. The $^{31}P\{^1H\}$ NMR spectrum displays two doublets of an AX spin system centered at 28.0 and 23.5 ppm (J(P,P) = 39 Hz).

Summary. We have demonstrated that reactions of aryl azides and molybdenum(0) complexes are facilitated by the presence of at least two labile ligands on molybdenum and a second, chelating donor on the aryl azide. The results of reactions of 8-AZQ and molybdenum(0) bis(phosphine) complexes are consistent with metal-mediated formation of phosphoranimine complexes occurring via chelate ring opening followed by intramolecular attack of a dangling phosphine on a bent-nitrene intermediate. The reaction of $[Mo(CO)_3(dppm)(CH_3CN)]$ and 8-AZQ results in formation of a phosphine–phosphoranimine chelate, $[Mo(CO)_3\{(Ph)_2PCH_2P(Ph)_2{=}NC_9H_6N\}]$ (**5a**). The crystal structure and IR data for **5a** are indicative of P–N π bonding in the phosphoranimine ligand.

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Supplementary Material Available: Complete listings of crystallographic data, atomic coordinates and equivalent isotropic displacement coefficients, bond lengths and angles, isotropic displacement coefficients, and H atom coordinates and isotropic displacement coefficients for molecules A and B of complex **5a** and a thermal ellipsoid plot of molecule B of complex **5a** (15 pages). Ordering information is given on any current masthead page.

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[19] (a) Wiegräbe, W.; Bock, H.; Lüttke, W. *Chem. Ber.* **1966**, *99*, 3737. (b) See refs 18a,e.