Poly(2-pyridyl)phosphines, PPy_nPh_{3-n} (n = 2, 3), and Their P-Substituted Derivatives as Tripodal Ligands in Molybdenum(0) Carbonyl Complexes

Juan A. Casares, Pablo Espinet,*,† Rosa Hernando, Gonzalo Iturbe, and Fernando Villafañe

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47005 Valladolid, Spain

Dianne D. Ellis and A. Guy Orpen‡

School of Chemistry, University of Bristol, Bristol BS8 1TS, U.K.

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The final products of the reactions of either $[Mo(CO)_6]$ or $[Mo(CO)_4(NBD)]$ (NBD = norbornadiene) with PPy_3 (Py = 2-pyridyl) or $ZPPy_3$ (Z = O, S, ClAu, C_6F_5Au) are *fac*-$[Mo(CO)_3(Py_3P\text{-}N_3)]$ or *fac*-$[Mo(CO)_3(Py_3PZ\text{-}N_3)]$, where the ligands act as tridentate N-donors. The use of $ZPPhPy_2$ (Z = O, S) leads to *fac*-$[Mo(CO)_3(ZPPhPy_2\text{-}Z,N_2)]$, the ligands acting as tridentate Z,N_2-donors. The crystal structure of *fac*-$[Mo(CO)_3(SPPhPy_2\text{-}S,N_2)]$ was determined by area detector diffractometry and shows that the coordination at molybdenum is essentially octahedral but with trigonal elongation. Some tetracarbonyl complexes which are intermediates in the formation of the above tricarbonyl complexes have been isolated (*cis*-$[Mo(CO)_4(PPy_3\text{-}P)_2]$ and *cis*-$[Mo(CO)_4(ZPPhPy_2\text{-}Z,N)]$ (Z = O, S)) or detected (*cis*-$[Mo(CO)_4(Py_3P\text{-}N_2)]$ and *cis*-$[Mo(CO)_4(SPPy_3\text{-}S,N)]$). The syntheses of the new complexes $[Au(C_6F_5)(PRPy_2\text{-}P)]$ (R = Py or Ph) are also described.

Introduction

Tripodal ligands are frequently used in coordination and organometallic chemistry as they allow tuning of the steric and electronic properties of the metal center. The interest in complexes containing tripodal ligands derives not only from structural aspects but also from their physical properties and their chemical behavior and particularly their catalytic activity. The ligands probably most extensively used for these purposes are anionic tripyrazolylborate ligands and their substituted derivatives,[1] whose chemistry resembles that of cyclopentadienyl ligands. The use of neutral tripodal ligands, such as triphosphines,[2] or those based on triazacyclononanes or trithiacyclononanes skeletons is also popular.[3,4] Polydentate ligands containing different donor atoms (socalled "hybrid" ligands) have recently received much attention.[5]

Among the phosphines containing pyridyl groups,[6] poly(2-pyridyl)phosphines PPy_nR_{3-n} (Py = 2-pyridyl, n = 2, 3) are good candidates to coordinate as tripodal ligands. In fact, several complexes where PPy_3 acts as a tridentate N-donor, such as $[M(Py_3P\text{-}N_3)_2]^{2+}$ (M = Fe, Ru, Co, Ni, Cu, Zn) are known.[7] Obviously, PPy_3 can also act as a P-donor ligand, or as P,N-donor (chelating or bridging), and these types of coordination have been reported when the ligand is attached to softer metals, such as low-valent Ru,[8] Os,[9] Rh,[10] Ir,[11] Pd,[12] Pt,[13] and the group

† E-mail: espinet@cpd.uva.es.
‡ E-mail: guy.orpen@bris.ac.uk.
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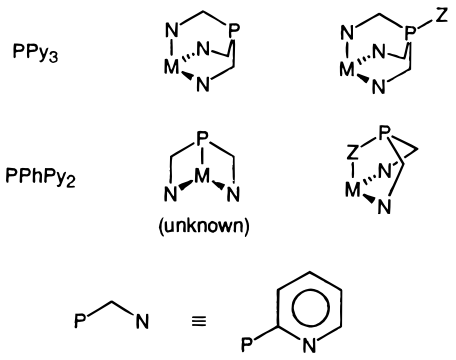
Chart 1



11 metals.[14] Thus, the hard−soft properties of the metal center apparently influence the behavior of the PPy_3 ligand in selecting the donor atom(s). Although clear-cut rules about the coordination mode of PPy_3 cannot yet be established, it seems evident that a tripodal N-donor coordination is not favored for soft metal centers.

Our purpose was to induce this type of coordination by quaternizing the phosphorus atom with noncoordinating or poorly coordinating substituents (Chart 1). The possible substituents at the phosphorus, Z, may be of widely ranging nature, and include an oxygen atom ($OPPy_3$) or even a metal fragment [$ML_n(PPy_3$-*P*)]. These new ligands are easily prepared and allow direction of the ligand behavior toward tripodal coordination regardless of the hardness of the metal center. On the other hand, this approach affords a family of ligands with different electronic properties but the same steric requirements, since the Z substituents are far from the metal. Such possibility is relatively rare for tripodal ligands, because tuning of their electronic properties is generally accomplished by changing the substituents attached (or very close) to the metal center, thereby also changing the steric requirements of the ligand.

Bis(2-pyridyl)phenylphosphine ($PPhPy_2$) also contains three donor atoms, but in this case tripodal coordination (P,N_2) would lead to formation of two very strained four-membered rings and is generally disfavored (Chart 1). To date this type of coordination has not been observed. In fact $PPhPy_2$ has the tendency to coordinate either as a P-donor or as a P,N-bridging ligand.[8,9,10b,11−15] In this case, the approach used before, i.e. the addition of a substituent blocking the phosphorus atom but itself having coordinating capability, may lead to more stable five-membered chelate rings (Chart 1) when the Z substituent is able to act as a coordinating ligand (e.g. $OPPhPy_2$), thus giving a tripodal coordination.

Here we report our studies of the reactions of PPy_3, $ZPPy_3$, and $ZPPhPy_2$ toward molybdenum(0) carbonyl complexes, aimed at investigation of the ability of these polydentate ligands to coordinate unfavorable soft metal centers. The Z substituents used (O, S, AuCl, and AuC_6F_5) were chosen because they produce neutral ligands (hence the presence of a counterion in the complexes is avoided), and they are easily synthesized starting from the phosphine.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of prepurified dinitrogen. Solvents were purified according to standard procedures.[16] $[Mo(CO)_4(NBD)]$,[17] (2-pyridyl)phosphines,[7c,10a] and their sulfides[18] were prepared as previously described. Phosphine oxides were prepared by standard methods,[19] and their spectroscopic and physical data compared to those reported.[18] [AuCl(PPy_3-*P*)] and [AuCl($PPhPy_2$-*P*)] were prepared by displacement of tetrahydrothiophene (tht) in [AuCl(tht)], although they had been previously reported starting from [AuCl(CO)].[14b] Reagents from commercial suppliers were used as received.

Table 1. Syntheses of *fac*-Tricarbonyl Complexes (mmol Used in the Reaction; Time (h); Yield

compound	from $[Mo(CO)_6]$	from $[Mo(CO)_4(NBD)]$
1	0.5; 17; 58	0.3; 48; 52
2a	0.3; 10; 61	0.3; 30; 57
2b	0.7; 5; 73	
2c		0.5; 24; 59
2d		0.25; 48; 63
3a	0.5; 3; 70	
3b	1; 2; 90	

The progress of the reactions involving carbonyl complexes was monitored by solution IR spectra in the 2100−1700 cm^{-1} region. Filtrations were carried out on dry Celite without exclusion of air. The products were air-stable solids unless otherwise stated, and were recrystallized at −20 °C.

Infrared spectra were recorded on a Perkin-Elmer 883 or 1720X apparatus in NaCl windows for solutions and Nujol mulls or KBr pellets for solids. NMR spectra were recorded on Bruker AC-300 or ARX-300 instruments in $CDCl_3$ at room temperature unless otherwise stated (with *J* values in Hz). NMR spectra are referred to TMS, 85% aqueous H_3PO_4, and $CFCl_3$. Elemental analyses were performed on a Perkin-Elmer 2400B microanalyzer. The visible spectra were recorded on a Shimadzu UV-160A apparatus.

[Au(C_6F_5)(PPy_3-*P*)]. A 100 mL flask is successively charged with 0.227 g of [Au(C_6F_5)(tht)][20] (0.5 mmol), 25 mL of toluene, and 0.133 g of PPy_3 (0.5 mmol). The white suspension is stirred at room temperature for 3 h. The volatiles are removed *in vacuo*, and the crude product is recrystallized from acetone, yielding 0.163 g (52%) of [Au(C_6F_5)(PPy_3-*P*)] as a white crystalline solid. ^{1}H NMR: δ 8.80 (d, J = 4.7, 3H), 8.03 (t, J = 6.9, 3H), 7.83 (m, 3H), 7.40 (m, 3H). $^{31}P\{^1H\}$ NMR: δ 42.5 (m). ^{19}F NMR: δ −116.1 (m, $2F_{ortho}$), −158.6 (t, J = 19.6, $1F_{para}$), −162.8 (m, $2F_{meta}$).

[Au(C_6F_5)($PPhPy_2$-*P*)]. A 100 mL flask is successively charged with 0.227 g of [Au(C_6F_5)(tht)][20] (0.5 mmol), 25 mL of toluene, and 0.132 g of $PPhPy_2$ (0.5 mmol). The white suspension is stirred at room temperature for 3 h. The volatiles are removed *in vacuo*, and the crude product is recrystallized from CH_2Cl_2/hexane, yielding 0.283 g (82%) of [Au(C_6F_5)($PPhPy_2$-*P*)] as a white crystalline solid. ^{1}H NMR: δ 8.78 (d, J = 4.8, 2H Py), 8.05 (ddd, J = 12.4, 7.7 and 1.4, 2H Ph), 7.91 (t, J = 6.5, 2H Py), 7.80 (m, 2H Py), 7.55 (m, 3H Ph), 7.38 (m, 2H Py). $^{31}P\{^1H\}$ NMR: δ 41.6 (m). ^{19}F NMR: δ −116.4 (m, $2F_{ortho}$), −158.6 (t, J = 19.9, $1F_{para}$), −162.7 (m, $2F_{meta}$).

General Method for the Preparation of the Tricarbonyl Complexes. A two-necked 100 mL flask is charged with acetonitrile (40 mL per mmol of reactants), either $[Mo(CO)_6]$ or $[Mo(CO)_4(NBD)]$, and equimolar amounts of the ligand. The mixtures are refluxed (for the $[Mo(CO)_6]$ case), or stirred at room temperature. A dark solid precipitates during the reaction. The quantities used in the reactions, times and yields are collected in Table 1. The workup procedure for each compound is described below.

***fac*-[$Mo(CO)_3$(Py_3P-N_3)], 1.** The deep purple solid was collected by filtration, washed with Et_2O (3 × 5 mL), dried under reduced pressure, and recrystallized from CH_2Cl_2/hexane. ^{1}H NMR: δ 9.47 (d, J = 5.5, 3H), 8.08 (dd, J = 11.4 and 7.4, 3H), 7.74 (t, J = 7.4,

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Table 2. Details of Crystal Structure Determination of **3b**

chem formula: $C_{19}H_{13}MoN_2O_3PS$	fw = 476.28
cryst syst: triclinic	space group: $P\bar{1}$ (No. 2)
a = 8.398(2) Å	T = 293(2) K
b = 9.275(2) Å	$\bar{\lambda}$ = 0.71073 Å
c = 14.936(3) Å	ρ(calcd) = 1.573 Mg/m^{-3}
α = 73.86(2)°	μ = 0.856 mm^{-1}
β = 81.33(2)°	transm coeffs = 0.839−0.916
γ = 64.219(12)°	R1[a] = 0.041
V = 1005.7(4) Å^3	wR2[a] = 0.084
Z = 2	

[a] Residuals calculated for reflections with $I > 2\sigma(I)$; wR2 = $[\sum w\Delta^2/\sum wF_o^4]^{0.5}$; $S = [\sum w\Delta^2/(N - NV)]^{0.5}$; R1 = $\sum||F_o| - |F_c||/\sum|F_o|$; $\Delta = F_o^2 - F_c^2$; N = NO + restraints; $w = [\sigma_c^2(F_o^2) + (gP)^2]^{-1}$, $\sigma_c^2(F_o^2)$ = variance in F_o^2 due to counting statistics, $P = [\max(F_o^2,0) + 2F_c^2]/3$.

3H), 7.20 (m, 3H). $^{31}P\{^1H\}$ NMR: δ −3.7 (s). IR (CH_2Cl_2): 1908 s, 1787 s (br) cm^{-1}. Visible (MeCN): 484 nm (ϵ = 6300).

***fac*-[Mo(CO)$_3$(Py$_3$PO-*N*$_3$)], 2a.** The mixture containing a purple solution and dark purple crystals was concentrated *in vacuo*, and cooled to −20 °C. The deep purple solid was collected by filtration, washed with Et_2O (3 × 5 mL), and dried under reduced pressure and *in vacuo*. ^1H NMR: δ 9.39 (d, J = 5.0, 3H), 8.39 (t, J = 6.8, 3H), 7.96 (m, 3H), 7.38 (m, 3H). $^{31}P\{^1H\}$ NMR: δ 1.2 (s). IR (CH_2Cl_2): 1915 s, 1803 s (br) cm^{-1}. Visible (MeCN): 483 nm (ϵ = 8400).

***fac*-[Mo(CO)$_3$(Py$_3$PS-*N*$_3$)], 2b.** The solvent was removed *in vacuo*, and the dark solid was recrystallized from CH_2Cl_2/hexane, giving dark purple crystals, which were isolated as for **2a**. ^1H NMR: δ 9.42 (d, J = 5.1, 3H), 8.77 (t, J = 5.5, 3H), 7.94 (m, 3H), 7.35 (m, 3H). $^{31}P\{^1H\}$ NMR: δ 24.3 (s). IR (CH_2Cl_2): 1915 s, 1800 s (br) cm^{-1}. Visible (MeCN): 493 nm (ϵ = 6300).

***fac*-[Mo(CO)$_3$(Py$_3$PAuCl-*N*$_3$)], 2c.** The dark purple solid obtained was collected by filtration, washed with MeCN (2 × 2 mL) and then with Et_2O (3 × 5 mL), and dried under reduced pressure and *in vacuo*. ^1H NMR: δ 9.46 (d, J = 4.5, 3H), 8.65 (m, 3H), 7.95 (m, 3H), 7.38 (m, 3H). $^{31}P\{^1H\}$ NMR: δ 35.6 (s). IR (CH_2Cl_2): 1915 s, 1805 s (br) cm^{-1}. Visible (MeCN): 514 nm (ϵ = 8900).

***fac*-[Mo(CO)$_3$(Py$_3$PAuC$_6$F$_5$-*N*$_3$)], 2d.** The dark purple solid obtained was collected by filtration, washed with Et_2O (3 × 5 mL), and dried under reduced pressure and *in vacuo*. ^1H NMR: δ 9.50 (d, J = 4.8, 3H), 8.70 (dd, J = 11.5 and 7.7, 3H), 7.97 (m, 3H), 7.39 (m, 3H). $^{31}P\{^1H\}$ NMR: δ 43.3 (m). ^{19}F NMR: δ −116.8 (m, 2F$_{ortho}$), −156.4 (t, J = 19.9, 1F$_{para}$), −161.7 (m, 2F$_{meta}$). IR (CH_2Cl_2): 1914 s, 1802 s (br) cm^{-1}. Visible (MeCN): 502 nm (ϵ = 5500).

***fac*-[Mo(CO)$_3$(Py$_2$PhPO-*N*$_2$,*O*)], 3a.** The solvent was removed *in vacuo*, and the dark oil was washed with Et_2O (2 × 10 mL) to give a dark purple solid, which was stored under dinitrogen at −20 °C. The complex is very air sensitive, and no satisfactory analyses could be obtained. The NMR spectra of **3a** showed a mixture of **3a**, **7a**, and $OPPhPy_2$ in an approximate ratio of 0.6/1/1. Some of the signals of the complexes could be assigned by dissolving each complex at low temperature after freezing the sample in a liquid dinitrogen bath and recording the spectra immediately after unfreezing, with the temperature at the NMR probe set at −60 °C. ^1H NMR: δ 9.44 (d, J = 5.4, 2H of **3a**), 9.21 (d, J = 5.2, 1H of **7a**), 8.84 (d, J = 4.4, 1H of **7a**), 8.78 (d, J = 4.5, 2H of $OPPhPy_2$), 8.71 (t, J = 7.1, 2H of **3a**), 8.29 (t, J = 6.9, 1H of **7a**), 8.10 (m), 7.98 (m, 1H of **7a**), 7.84 (m), 7.51 (m), 7.13 (m). $^{31}P\{^1H\}$ NMR: δ 19.0 (s). IR (MeCN): 1925 s, 1799 s (br) cm^{-1}.

***fac*-[Mo(CO)$_3$(Py$_2$PhPS-*N*$_2$,*S*)], 3b.** The dark purple solid obtained was cooled at −20 °C and then collected by filtration, washed with Et_2O (3 × 10 mL), and dried under reduced pressure and *in vacuo*. ^1H NMR: δ 9.40 (d, J = 5.2, 2H), 8.25 (d, J = 13.0, 1H), 8.22 (dd, J = 13.1 and 1.6, 1H), 7.92 (m, 3H), 7.73 (m, 2H), 7.61 (dd, J = 7.6 and 6.7, 2H), 7.30 (m, 2H). $^{31}P\{^1H\}$ NMR: δ 16.4 (s). IR (CH_2Cl_2): 1919 s, 1818 s, 1794 s cm^{-1}. Visible (MeCN): 471 nm (ϵ = 3000).

X-ray Crystallographic Analysis of 3b. Many of the details of the structure analysis are listed in Table 2. X-ray diffraction measurements on single crystals mounted in a thin-walled glass capillary were made with graphite monochromated Mo Kα X-radiation ($\bar{\lambda}$ = 0.710 73 Å) using a Siemens SMART[21] area detector diffractometer at room temperature. A full hemisphere of reciprocal space was scanned by 0.3° ω steps at ϕ = 0, 88 and 180° with the area detector center held at 2θ = −27°. Intensity data were integrated[22] for 2θ < 50.0° and corrected for Lorentz, polarization, and absorption effects on the basis of symmetry equivalent relection data. The structure was solved by Patterson methods, and refined by full-matrix least-squares against F^2 against all data with $I > -3\sigma(I)$ with weights, w, set equal to $[\sigma_c^2(F_o^2) + (aP)^2 + bP]^{-1}$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$ and a and b were assigned values given in Table 2. All non-hydrogen atoms heavier than carbon were refined without positional constraints and assigned anisotropic displacement parameters. Phenyl rings were constrained to idealized geometry and all carbon atoms assigned isotropic displacement parameters. All hydrogen atoms were assigned fixed isotropic displacement parameters and were constrained to ideal geometries. Final difference syntheses showed no chemically significant features. Refinements converged to residuals given in Table 2. Complete atomic coordinates, thermal parameters, bond distances, and angles have been included in the Supporting Information. All calculations were made with programs of the SHELXTL-PLUS system.[23] Complex neutral-atom scattering factors were taken from ref 24.

***cis*-[Mo(CO)$_4$(PPy$_3$-*P*)$_2$], 4.** A 100 mL Schlenk flask was successively charged with 0.106 g of PPy_3 (0.4 mmol), 0.060 g of [Mo(CO)$_4$(NBD)] (0.2 mmol), and 15 mL of CH_2Cl_2. The solution was stirred at 0 °C for 16 h, and toluene (10 mL) was added. Concentration of the solution *in vacuo* and cooling to −20 °C gave pale pink crystals, which were washed with Et_2O (3 × 3 mL) and dried *in vacuo*, yielding 0.073 g (49%) of **4**. ^1H NMR: δ 8.47 (d, J = 4.4, 6H), 7.73 (d, J = 7.7, 6H), 7.52 (m, 6H), 7.10 (m, 6H). $^{31}P\{^1H\}$ NMR: δ 49.7 (s). IR (CH_2Cl_2): 2027 m, 1934 s, 1919 vs, 1888 m cm^{-1}.

***cis*-[Mo(CO)$_4$(Py$_3$P-*N*$_2$)], 5.** This complex was detected when equimolar amounts of [Mo(CO)$_4$(NBD)] and PPy_3 were dissolved in CH_2Cl_2 or $CDCl_3$ at room temperature. ^1H NMR:[25] δ 9.19 (d, J = 5.5, 2H coordinated Py), 9.02 (d, J = 4.7, 1H uncoordinated Py), 8.18 (t, J = 7.8, 1H uncoordinated Py), 8.00 (m, 1H uncoordinated Py), 7.52 (o, 3H: 2H of coordinated Py, 1H of uncoordinated Py), 7.10 (o, 2H coordinated Py), 6.95 (d, J = 6.0, 2H coordinated Py). $^{31}P\{^1H\}$ NMR: δ −10.5 (s). IR (CH_2Cl_2): 2012, o, o, 1839 cm^{-1} (o = overlapped with signals of other complexes present in the mixtures).

***cis*-[Mo(CO)$_4$(SPy$_3$-*S*,*N*)], 6.** This complex was detected when equimolar amounts of [Mo(CO)$_4$(NBD)] and $SPPy_3$ were dissolved in CH_2Cl_2 or $CDCl_3$ at room temperature. ^1H NMR: δ 9.28 (d, J = 4.6, 1H), 8.7 (o, 2H), 8.21 (t, J = 7.3, 2H), 7.9 (o, 3H), 7.8 (o, 1H), 7.50 (m, 2H), 7,4 (o, 1H). $^{31}P\{^1H\}$ NMR: δ 36.0 (s). IR (CH_2Cl_2): 2019, 1913, o, 1835 cm^{-1} (o = overlapped with signals of other complexes present in the mixtures).

Synthesis of *cis*-[Mo(CO)$_4$(Py$_2$PhPO-*N*,*O*)], 7a. A 100 mL Schlenk flask was successively charged with 0.140 g of $OPPhPy_2$ (0.5 mmol), 0.150 g of [Mo(CO)$_4$(NBD)] (0.5 mmol), and 20 mL of toluene. The brown solution was stirred for 2 h at room temperature, during which time a yellowish green solid precipitated. The solution was decanted off, and the solid was washed with Et_2O (3 × 5 mL) and dried *in vacuo*, yielding 0.153 g (**63%**) of **7a**. As for **3a**, **7a** is very air-sensitive and a satisfactory analysis could not be obtained. The NMR spectra of **7a** showed the same mixture as that found for **3a** (see above). $^{31}P\{^1H\}$ NMR: δ 34.4 (s). IR (CH_2Cl_2): 2019 m, 1908 s, 1885 vs, 1826 m cm^{-1}.

Synthesis of *cis*-[Mo(CO)$_4$(Py$_2$PhPS-*N*,*S*)], 7b. A 100 mL Schlenk flask containing 20 mL of toluene was cooled in an ice bath, and successively charged with 0.148 g of $SPPhPy_2$ (0.5 mmol) and 0.150 g of [Mo(CO)$_4$(NBD)] (0.5 mmol). The mixture was stirred at 0 °C for 72 h and then filtered to remove a dark precipitate of **3b**. Successive

(21) SMART Siemens Molecular Analysis Research Tool V4.014 copyright 1989−94, Siemens Analytical X-ray, Madison, WI.
(22) SAINT (Siemens Area detector INTegration) program, Siemens Analytical X-ray, Madison, WI.
(23) SHELXTL-PLUS Rev. 5.0, Siemens Analytical X-ray, 1994.
(24) *International Tables for Crystallography*; Kluwer: Dordrecht, The Netherlands, 1992; Vol. C.
(25) ^1H NMR of [Mo(CO)$_4$(Py$_2$PhP-*N*$_2$)][15a] recorded at 300 MHz: δ 9.22 (d J = 5.5, 2H Py), 7.80 (t, J = 8.5, 2H Ph), 7.67 (m, 3H Ph), 7.54 (tt, J = 7.8 and 1.7, 2H Py), 7.11 (t, J = 5.8, 2H Py), 7.07 (d, J = 7.9, 2H Py).

crystallizations of the filtrate lead to several batches of **3b** and finally to a brown crystalline solid, which was decanted, washed with hexane (3 × 5 mL), and dried *in vacuo*, yielding 0.079 g (57%) of **7b**. ^{1}H NMR: δ 9.27 (d, J = 4.8, 1H), 8.72 (d, J = 4.7, 1H), 8.46 (t, J = 7.6, 1H), 7.99 (m, 1H), 7.75 (m, 3H), 7.58 (m, 5H), 7.36 (m, 1H). ^{31}P{^{1}H} NMR: δ 40.4 (s). IR (CH_2Cl_2): 2019 m, 1913 s, 1886 vs, 1836 m cm^{-1}.

Results and Discussion

All the $ZPPhPy_2$ and $ZPPy_3$ ligands had been previously described,[14b,18] except the (pentafluorophenyl)gold complexes, which are synthesized by displacement of tetrahydrothiophene (tht) from [Au(C_6F_5)(tht)] in toluene at room temperature (see Experimental Section).

The *fac*-tricarbonyl complexes [Mo(CO)$_3$(Py_3P-N_3)], **1**, and [Mo(CO)$_3$(Py_3PZ-N_3)], (Z = O, **2a**; S, **2b**; AuCl, **2c**; AuC_6F_5, **2d**) were obtained by treating either [Mo(CO)$_6$] or [Mo(CO)$_4$(NBD)] with equimolar amounts of the appropriate ligand PPy_3 or $ZPPy_3$. When [Mo(CO)$_6$] was used as starting material, the reactions had to be carried out in refluxing acetonitrile to favor the release of carbon monoxide. Starting from [Mo(CO)$_4$(NBD)], the substitution process is achieved smoothly at room temperature. The latter method was preferred for the gold-containing phosphines, to avoid their decomposition to give metallic gold (see Experimental Section for details). When Z = O, S, $ZPPhPy_2$ species might act also as tripodal ligands, as indicated in Chart 1. In fact, the reaction of molybdenum(0) substrates with [AuCl($PPhPy_2$-*P*)] or [Au(C_6F_5)($PPhPy_2$-*P*)] led to decomposition products, including metallic gold, whereas reactions with $OPPhPy_2$ or $SPPhPy_2$ allowed the syntheses of *fac*-[Mo(CO)$_3$($ZPPhPy_2$-*Z*,N_2)], (Z = O, **3a**; S, **3b**).

Complexes **1**, **2**, and **3** are very dark crystalline solids, sparingly soluble in organic solvents. Their *fac* geometry is evidenced by the C−O stretching absorptions detected in their IR spectra (see Experimental Section). These spectra show another interesting feature: in complexes **2a** and **2b**, those containing phosphine chalcogenides, there is only a small variation of the P═E stretching frequency (1238 cm^{-1} in **2a**, 667 cm^{-1} in **2b**) with respect to the free ligands (1214 cm^{-1} for P═O, 662 cm^{-1} for P═S). This indicates that the chalcogen atom is not coordinated to the metal.[26] Therefore, a tridentate N-donor coordination of the phosphine chalcogenide ligands is inferred from the IR data. For complexes **3**, no absorptions are found in the ν(P═E) range for the free ligand, implying in this case the coordination of the chalcogen atom. Assignment of the corresponding ν(P═E) wavenumber is made very difficult because of the presence of many other bands in the expected ranges.

The ^{1}H NMR spectra of **1**, **2**, and **3** show the expected equivalence of the three Py groups: only four signals of equal intensity due to the four different hydrogens present in the heterocycle are observed for **1** and **2**. In complexes **3**, the equivalence of the H^6 hydrogens (those appearing at lower field) of both Py groups is also evident in their ^{1}H NMR spectra. Complex **3a** could not be completely characterized, as it rapidly decomposes in solution giving rise to additional signals of [Mo(CO)$_4$($OPPhPy_2$-*O*,*N*)] (**7a**, see later) and free $OPPhPy_2$. The ^{31}P{^{1}H} NMR spectrum of **3a** could only be assigned by preparing the NMR sample in a liquid nitrogen bath, and allowing melting and simultaneous dissolution at temperatures below −60 °C. The weak bond between the soft molybdenum(0) center and the hard oxygen atom in the ligand must presumably be responsible for the instability observed for **3a** and for the rest of complexes reported here containing a molybdenum(0)−oxygen bond.

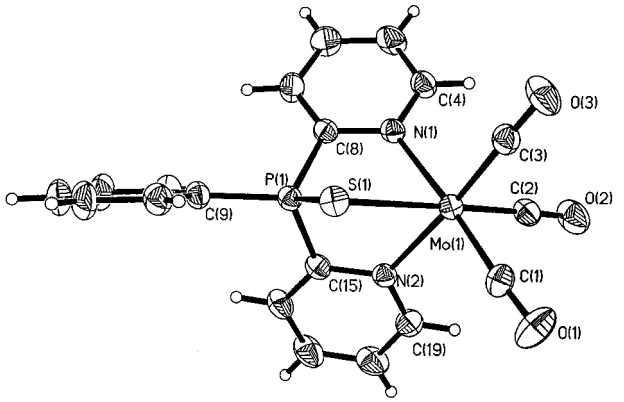

Figure 1. Molecular structure of **3b** showing the labeling scheme. All hydrogen atoms have been omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) from the Crystal Structure of **3b**

Mo(1)−C(2)	1.927(5)	Mo(1)−S(1)	2.6242(14)
Mo(1)−C(1)	1.930(5)	P(1)−C(9)	1.797(5)
Mo(1)−C(3)	1.941(5)	P(1)−C(15)	1.820(5)
Mo(1)−N(2)	2.274(4)	P(1)−C(8)	1.825(4)
Mo(1)−N(1)	2.281(4)	P(1)−S(1)	1.973(2)
C(2)−Mo(1)−C(1)	83.7(2)	C(9)−P(1)−C(8)	111.2(2)
C(2)−Mo(1)−C(3)	86.7(2)	C(15)−P(1)−C(8)	102.0(2)
C(1)−Mo(1)−C(3)	87.7(2)	C(9)−P(1)−S(1)	116.3(2)
C(2)−Mo(1)−N(2)	96.2(2)	C(15)−P(1)−S(1)	108.9(2)
C(1)−Mo(1)−N(2)	95.4(2)	C(8)−P(1)−S(1)	108.0(2)
C(3)−Mo(1)−N(2)	175.9(2)	P(1)−S(1)−Mo(1)	85.43(5)
C(2)−Mo(1)−N(1)	97.5(2)	C(4)−N(1)−C(8)	117.2(4)
C(1)−Mo(1)−N(1)	177.6(2)	C(4)−N(1)−Mo(1)	122.6(3)
C(3)−Mo(1)−N(1)	94.5(2)	C(8)−N(1)−Mo(1)	120.2(3)
N(2)−Mo(1)−N(1)	82.33(13)	C(19)−N(2)−C(15)	117.0(4)
C(2)−Mo(1)−S(1)	177.9(2)	C(19)−N(2)−Mo(1)	122.9(3)
C(1)−Mo(1)−S(1)	97.18(14)	C(15)−N(2)−Mo(1)	120.1(3)
C(3)−Mo(1)−S(1)	95.23(14)	O(1)−C(1)−Mo(1)	177.1(4)
N(2)−Mo(1)−S(1)	81.82(9)	O(2)−C(2)−Mo(1)	175.8(5)
N(1)−Mo(1)−S(1)	81.62(9)	O(3)−C(3)−Mo(1)	178.6(5)
C(9)−P(1)−C(15)	109.4(2)		

A crystallographic study of **3b** was undertaken, since this type of structure is not frequent in the literature. To our knowledge there is only one report of a crystallographically characterized SPR_3-*S* ligand coordinated to molybdenum(0).[27] On the other hand, complexes with N_2,*S*-tripodal ligands are scarce,[5a−e] and only one X-ray structure has been reported of a molybdenum(0) complex containing 1,3-bis(2-pyridyl)-1-thiapropane.[5c] The crystal structure of **3b** was determined by area detector diffractometry. Figure 1 shows the molecular strucutre of the complex in the crystal and Table 3 gives important structural parameters. Molybdenum−CO bond lengths are slightly shorter than usual,[28] reflecting the poor π-acceptor character of the tripod ligand. As expected the molybdenum is octahedrally coordinated with small deviations from ideal coordination geometry. The largest deviations from ideal geometry involve the tripod ligand for which the S−Mo−N and N−Mo−N angles are systematically *ca.* 82°. Similarly the OC−Mo−CO angles are also less than the ideal values (mean 86.0°), while the S−Mo−C and N−Mo−C angles are >90°. Therefore the coordination at molybdenum is trigonally elongated. It is interesting to compare the geometry of the

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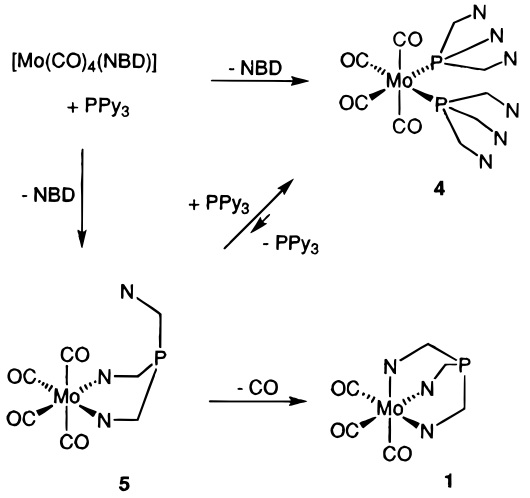
(28) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1-S83.

Scheme 1

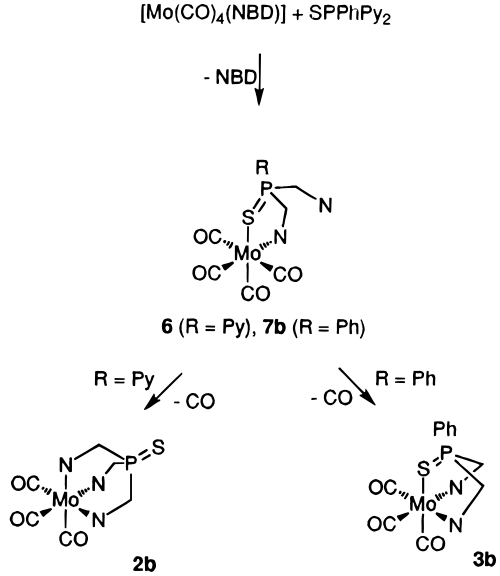


coordinated $SPPhPy_2$ ligand in **3b** with that found in $[Pd(C_6F_5)Br(SPPhPy_2\text{-}S,N)]$, recently reported by us.[29] All the distances and angles are very similar in both complexes and show similar values to those reported for other SPR_3 complexes,[26b,30] except the M−S−P angle (85.43(5)°) which is noticeably lower than that found in the palladium(II) complex (94.23(2)°)[29] or to those in other SPR_3-*S* complexes (96−120°).[31] This must be a consequence of the tripodal coordination of the $SPPhPy_2$ ligand in **3b**.

Some intermediates in the formation of **1**, **2**, and **3** can be detected or isolated in additional experiments. Thus, the *cis*-tetracarbonyl species $[Mo(CO)_4(PPy_3\text{-}P)_2]$ (**4**) and $[Mo(CO)_4(Py_3P\text{-}N_2)]$ (**5**) are detected by IR and NMR spectroscopy during the reaction of equimolar amounts of $[Mo(CO)_4(NBD)]$ and PPy_3, which finally leads to **1**. Complex **4** was isolated in a 49% yield when this reaction was carried out with a Mo/PPy_3 ratio of 1/2 at 0 °C in dichloromethane. The complex shows ν(CO) bands and a ^{31}P chemical shift (Experimental Section) similar to those observed for *cis*-tetracarbonyl complexes with $PPhPy_2$,[15a] and with other PR_3 complexes.[32,33] The ^1H NMR spectrum shows the expected equivalence of all the pyridyl groups (see Experimental Section). Complex **5** could not be isolated as a solid, but the NMR and IR data of mixtures of $[Mo(CO)_4(NBD)]$ and PPy_3 (1/1) indicated its presence. The $^{31}P\{^1H\}$ NMR and IR spectra of **5** (see Experimental Section) is very similar to those of the previously reported $[Mo(CO)_4(Py_2PhP\text{-}N_2)]$.[15a] The N_2-chelating coordination of the ligand is also supported by the ^1H NMR spectrum, which is invariant down to −60 °C, thus discounting possible dynamic process involving other types of coordination, such as P,N-chelation.

When the reaction of $[Mo(CO)_4(NBD)]$ and PPy_3 (1/1) is monitored by IR and NMR spectroscopy, a qualitative picture of the reaction can be obtained, shown in Scheme 1. Initially, approximately equal amounts of **4** and **5** are formed, but then the concentration of **4** slowly increases while that of **5** remains practically constant. This suggests that **4** is being formed not only by substitution of the NBD ligand, but also from **5**, by

Scheme 2



substitution of the PPy_3-N_2 ligand (it is known that $[Mo(CO)_4(Py_2PhP\text{-}N_2)]$ similarly decomposes slowly to *cis*-$[Mo(CO)_4(PPhPy_2\text{-}P)_2]$);[15a] since **5** is being formed from $[Mo(CO)_4(NBD)]$, a roughly constant concentration is maintained for some time. Eventually the slowest process, removal of CO from **5**, drives the reaction irreversibly to the final product, **1**.

In the reactions of $[Mo(CO)_4(NBD)]$ with $ZPPy_3$ or $ZPPhPy_2$ to give **2** or **3**, respectively, the initial products are *cis*-$[Mo(CO)_4(ZPRPy_2\text{-}Z,N)]$ (R = Py, Z = S, **6**; R = Ph, Z = O, **7a**, or S, **7b**), as shown in Scheme 2, which then undergo decarbonylation to the final products. Only **7b** could be isolated and throughly characterized, by reacting equimolar amounts of $[Mo(CO)_4(NBD)]$ and $SPPhPy_2$ in toluene at 0 °C. Even at 0 °C some decarbonylation occurs, which process becomes rapid when **7b** is dissolved at room temperature. The structure proposed for **7b** is supported by its IR spectrum (*cis*-tetracarbonyl CO bands and lack of bands due to noncoordinated P═S). The ^1H NMR spectrum (Experimental Section) shows, as expected, two H^6 signals for the two, coordinated (δ 9.27) and noncoordinated (δ 8.72), inequivalent pyridyl groups.

Only crude samples of *cis*-$[Mo(CO)_4(OPPhPy_2\text{-}O,N)]$, **7a**, could be obtained as a yellowish green solid. As in the case of **3a**, the high instability of **7a**, associated with O-coordination, precluded its characterization in solution but the proposed geometry is supported by the data available: *cis*-tetracarbonyl bands and lack of noncoordinated ν(P═O) band in the IR spectrum, and two H^6 signals due to two inequivalent Py groups in the ^1H NMR spectrum (δ 9.21, coordinated; δ 8.84, noncoordinated).

Finally, the study of the reaction of $[Mo(CO)_4(NBD)]$ with the $ZPPy_3$ ligands only allowed the detection, but not the isolation, of the tetracarbonyl intermediate *cis*-$[Mo(CO)_4(SPPy_3\text{-}S,N)]$, **6**, by IR monitoring at 0 °C and NMR at −20 °C. This compound rapidly converts into the tricarbonyl **2b**.

Complexes **1**, **2**, and **3** have the same *fac*-geometry, thus allowing spectroscopic evaluation of the donating properties of the various ligands. In principle, their visible spectra could supply some information about these properties, since the high extinction coefficient for the absorptions detected indicate that they are mostly metal to ligand charge transfer bands. However, there is controversy in trying to correlate the energy of these absorptions and the π-accepting capability of the ligands, even for well-studied systems, such as $[Mo(CO)_4(\alpha\text{-diimine})]$ (M = Cr, Mo, W).[34]

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(33) See, for example: Andrews, G. T.; Colquhoun, I. J.; McFarlane, W.; Grim, S. O. *J. Chem. Soc., Dalton Trans.* **1982**, 2353−2358.

On the other hand, the donor−acceptor balance (rather than the π-acceptor capability) of the ligands can be easily evaluated from their C−O stretching frequencies, since strong donor and/or weak acceptor ligands should weaken the C−O bonds more and *vice versa*. The observed ν(CO) values (see Experimental Section) support the following sequence from strong donor/weak acceptor to weak donor/strong acceptor ligands: PPy_3 > $ZPPy_3$ > $ZPPhPy_2$. As it is to be expected, the strongest donor/weakest acceptor ligand is the phosphine PPy_3. Oxidation or Au coordination of the phosphorus atom renders the Py moieties more weakly donating, curiously to about the same extent. The $ZPPhPy_2$ ligands are apparently the worst donors when tripodally coordinated.

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Supporting Information Available: Tables of elemental analyses and IR data, and for the crystal structure of **3b**, complete tables of atomic coordinates, thermal parameters, bond distances and angles, and details of the structure analysis (8 pages). Ordering information is available on any current masthead page.

IC960645T

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