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Phenylbis(2-pyridyl)phosphine: *P*- vs. *N,N'*-coordination in carbonylmolybdenum-(0) and -(II) complexes

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Abstract

The first carbonyl molybdenum-(0) and -(II) complexes with phenylbis(2-pyridyl)phosphine (PPhpy₂) have been synthesized. PPhpy₂ reacts with [Mo(CO)₅(NCMe)] to give [Mo(CO)₅(PPhpy₂-*P*)]. With [Mo(CO)₄(NBD)] (NBD = norbornadiene) it gives [Mo(CO)₄(PPhpy₂-*P*)₂] when a 2:1 ratio is used, or [Mo(CO)₄(py₂PhP-*N,N'*)] for a 1:1 ratio. Decarbonylation of any of these pyridylphosphine complexes leads to an oligomer of formula [Mo(CO)₃(μ-PPhpy₂)_n], which is also obtained after heating [Mo(CO)₆] in solution with an equimolar amount of PPhpy₂. The oligomer undergoes oxidative addition by iodine or allylbromide to give [MoI₂(CO)₃(py₂PhP-*N,N'*)], or [MoBr(η³-CH₂CHCH₂)(CO)₂(py₂PhP-*N,N'*)], respectively. These complexes are also obtained by addition of equimolar amounts of PPhpy₂ to solutions of [MoI₂(CO)₃(NCMe)₂] and MoBr(η³-CH₂CHCH₂)(CO)₂(NCMe)₂, respectively. The ligand tends to act as a *P*-donor towards molybdenum(0) substrates, and as a chelating *N,N'*-donor in molybdenum(II) complexes.

1. Introduction

Phenylbis(2-pyridyl)phosphine (PPhpy₂) (Fig. 1) may coordinate as phosphorus and/or nitrogen donor, acting as monodentate, bidentate (chelating or bridging), or tridentate (bridging). In its bridging modes, it may stabilize dimers, or even oligomers and polymers. Moreover, the different electronic properties of the donor atoms, *i.e.* the “soft” phosphorus *vs.* the “hard” nitrogens, may determine its ligand behaviour depending on the hardness of the metal centre.

In spite of these promising properties, there are very few reports of the use of PPhpy₂ as a ligand. In fact, only rhodium [1], copper, silver [2], and gold [3] complexes have been so far reported, in contrast with the extensive use of diphenyl(2-pyridyl)phosphine as bridging ligand [4*]. Our group is studying the behaviour of PPhpy₂ and some of its derivatives toward different metals, such as palladium, platinum [5], and molybde-

num. The first carbonylmolybdenum complexes containing PPhpy₂ are reported here. This metal was chosen since different oxidation states are easily available, with different degrees of hardness.

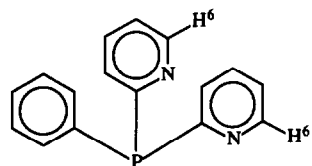
2. Results and discussion

The reactions studied are summarized in Scheme 1. Analytical and most relevant spectroscopic data are collected in Table 1. Other spectroscopic data are given in the Experimental section.

The addition of an equimolar amount of PPhpy₂ to a dichloromethane solution of [Mo(CO)₅(NCMe)], prepared *in situ* from [Mo(CO)₆] and Me₃NO in MeCN, gives [Mo(CO)₅(PPhpy₂-*P*)], **1**, in *ca.* 75% yield ((i), Scheme 1). The stoichiometry for this complex is confirmed by the IR spectrum in the C–O stretching region, which is that expected for a pentacarbonyl complex, and by C,H,N analyses (Table 1). The coordination of the ligand through the phosphorus atom is shown by the ³¹P{¹H} NMR spectrum of **1**, with a singlet at δ 44.3 ppm, compared to δ – 2.5 ppm (CDCl₃ solution) for the free donor. In contrast, the ¹H NMR spectrum of **1** does not provide much information

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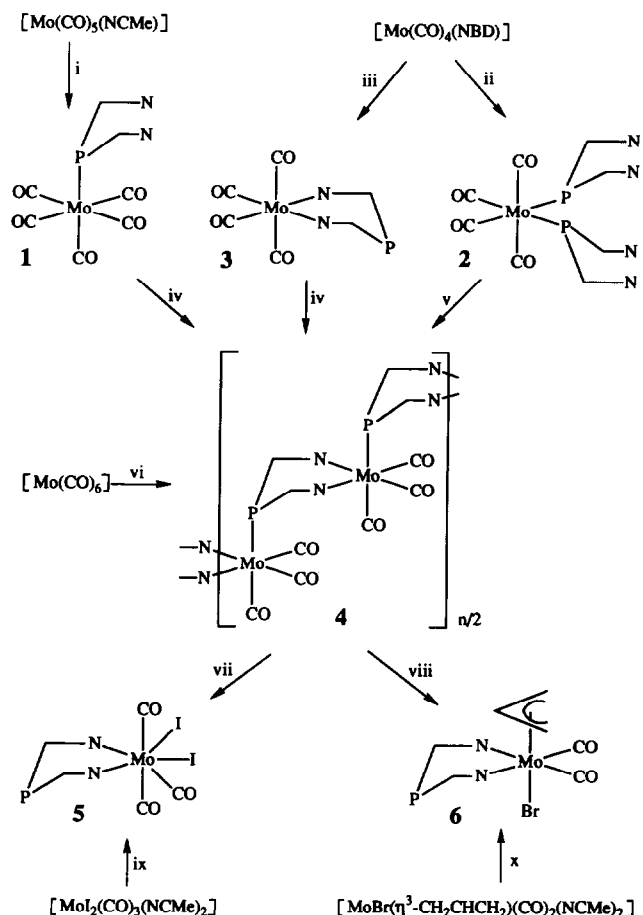
* Reference number with asterisk indicates a note in the list of references.

Fig. 1. Representations of phenylbis(2-pyridyl)phosphine (PPhpy₂).

about the geometry of the complex, since the spectrum is little changed by coordination: a broad doublet assigned to H⁶ in the pyridine moieties (see Fig. 1), which appears downfield of the unresolved multiplet due to the rest of the hydrogen atoms of the ligand, is common to most of the complexes described here.

The PPhpy₂ ligand also coordinates through the phosphorus atom when two equivalents react with [Mo(CO)₄(NBD)]. The reaction was carried out in toluene at room temperature (r.t.), and *cis*-[Mo(CO)₄-(PPhpy₂-P)₂], **2**, precipitated as an off-white solid ((ii), Scheme 1). The IR spectrum of **2** in the C–O stretching region showed the pattern expected for a *cis*-tetracarbonyl complex (Table 1), with frequencies similar to those of *cis*-[Mo(CO)₄-(PPh₃)₂][6*]. The ³¹P{¹H} NMR spectrum of **2** shows a singlet at δ 44.6 ppm, a chemical shift very similar to that of **1** (Table 1), and to the values reported for compounds such as [Mo(CO)₅-(PR₃)], and [Mo(CO)₄(PR₃)₂][7*]. All these data support the *P*-coordination of two phosphines per metal atom. In the ¹H NMR spectrum of **2**, the protons labelled as H⁶ now appear 0.4 ppm upfield with respect to those of **1**.

When compound **2** was kept in solution at r.t. for several hours, both the IR and the NMR spectra revealed additional signals, assigned to **1** and to other unidentified products. It is noteworthy that the reaction of [Mo(CO)₄(NBD)] and two equivalents of PPhpy₂ in solvents other than toluene (such as CH₂Cl₂ or



Scheme 1. Reactions carried out in this work: (i) PPhpy₂, –MeCN; (ii) **2** PPhpy₂, –NBD; (iii) PPhpy₂, –NBD; (iv) –CO; (v) –CO, –PPhpy₂; (vi) PPhpy₂, –CO; (vii) I₂; (viii) CH₂=CHCH₂Br; (ix) and (x) PPhpy₂, –MeCN.

THF) directly yields a similar mixture of products; thus, the precipitation of **2** during the reaction is the main factor allowing its isolation. The mixture of prod-

TABLE 1. IR, ³¹P{¹H} NMR and analytical data for the compounds described in this work

Compd.	IR ^a	³¹ P{ ¹ H} NMR ^b	%C ^c	%H ^c	%N ^c
1	2074m, 1997w, 1959vssh, 1954vs ^d	44.3 ^e	50.74 (50.41)	2.67 (2.62)	5.53 (5.60)
2	2024m, 1928vs, 1914vssh, 1883m	44.6 ^e	59.04 (58.70)	3.56 (3.57)	7.65 (7.61)
3	2012m, 1902vs, 1884ssh, 1838s	–9.7 ^f	50.53 (50.86)	2.69 (2.78)	5.73 (5.93)
4	1927vs, 1838s, 1796s	51.8	51.03 (51.37)	3.02 (2.96)	6.18 (6.31)
5	2042s, 1985vs, 1937m	–11.5 ^f	32.86 (32.69)	1.92 (1.88)	3.82 (4.01)
6	1946vs, 1851s	–9.4 ^f	46.53 (46.85)	3.43 (3.38)	4.96 (5.12)

^a Data in cm^{–1}, CH₂Cl₂ solution unless otherwise stated. ^b Data in ppm referred to 85% aq. H₃PO₄ as external reference, spectra recorded at 121.5 MHz in CDCl₃ solution unless otherwise stated. ^c Found values, calculated values in parentheses. ^d Hexane solution. ^e CD₂Cl₂ solution.

^f Spectra recorded at 32.4 MHz.

ucts formed by **2** in solution could be due both to the relative bulkiness of the phosphine, and to the presence of uncoordinated nitrogen atoms. It is known that compounds of the type *cis*-[Mo(CO)₄(PR₃)₂] thermally isomerize to the *trans* form by a dissociative mechanism, this process being faster for bulkier ligands [6a*]. This suggests that PPhpy₂ should dissociate easily, since its cone angle (when acting as *P*-donor) is expected to be very similar to that of PPh₃, which has a fast dissociation rate in *cis*-[Mo(CO)₄(PPh₃)₂] [6a*].

The fact that PPhpy₂ is a *P*-donor in the reactions described above, *i.e.* when enough ligand is added to replace the weak MeCN or NBD ligands, led us to study the reaction of the pyridylphosphine with [Mo(CO)₄(NBD)] in equimolar amounts, as the presence of two available coordination positions in this complex might favour coordination of the pyridine moieties. This reaction ((iii), Scheme 1), carried out in CH₂Cl₂ at r.t., leads to a mixture of products, which includes **1**, **2**, and **3**, as shown by IR monitoring. Red crystals of *cis*-[Mo(CO)₄(py₂PhP-*N,N'*)], **3**, were separated by crystallization from the mixture in *ca.* 30% yield.

The coordination of the phosphine in this case by *N,N'*-chelation was supported by both NMR and IR data. The ³¹P{¹H} NMR spectrum of **3** (Table 1) indicated the non-coordination of the phosphorus atom, since it showed a singlet at δ -9.7 ppm, in the same region than that of the free donor. The proton atoms labelled H⁶ (Fig. 1) appeared in the ¹H NMR spectrum at δ 9.21 ppm, as reported for PPhpy₂ acting as an *N,N'*-donor [1]. The IR spectrum of **3** in the C–O stretching region (Table 1) shows a *cis*-tetracarbonyl pattern, with frequencies lower than those of **2**, and similar to those reported for [Mo(CO)₄(bipy)] [6b*,8]. Furthermore, complex **3** is red, just as [Mo(CO)₄(bipy)] [8], whereas **1** and **2** are pale coloured, as reported for [Mo(CO)₄(PR₃)L] (L = CO or PR₃) [9]. The stoichiometry of **3** was confirmed by its mass spectrum and by C,H,N analyses (see Experimental section).

Although **3** could be selectively separated from the reaction mixture, the isolated compound is unstable. Monitoring solutions of **3** by IR and NMR spectroscopies showed decomposition of **3** mainly to give **1**, **2**, and some **4**; this decomposition was very extensive after two days in solution at r.t. and also takes place in the solid state, where the red crystals slowly change to a greenish powder containing **1** and other unidentified products. These results indicate that the chelating effect hardly compete with the tendency of PPhpy₂ to act as *P*-donor in molybdenum(0) complexes, and prompted us to determine which is the final decomposition product of the process when released CO is evacuated from the system. Thus **3** was heated under

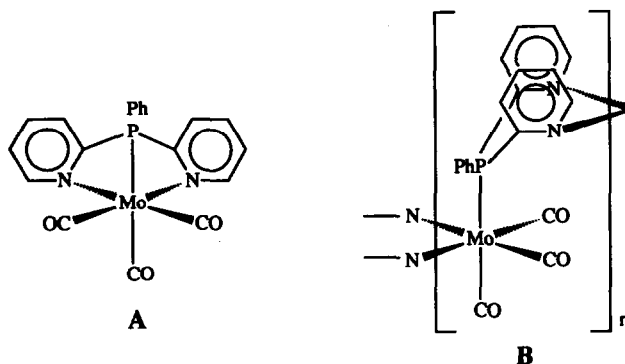


Fig. 2. Two possible coordination geometries for compound **4**.

reflux in toluene, affording a yellow-orange insoluble solid, **4**. The same compound was obtained on heating **2**, **1**, or equimolar mixtures of [Mo(CO)₆] and PPhpy₂ under reflux in toluene ((iv), (v), and (vi), Scheme 1). In the case of **2**, PPhpy₂ was found in the remaining toluene solution, C,H,N analyses of the yellow-orange solid agree with the stoichiometry “Mo(CO)₃(PPhpy₂)”, and IR spectra suggest a *fac* arrangement of the carbonyls. The ¹H NMR data again support the coordination of the nitrogen atoms, since the downfield broad doublet appears at δ 9.00 ppm [1].

Figure 2 shows the two possible coordination modes of PPhpy₂ which are consistent with these data. Tridentate chelating coordination **A**, giving rise to a monomer, has been found for the related ligand (NH₂CH₂CH₂CH₂)₂PPh in octahedral complexes [10], but not for PPhpy₂, which should give rise to two very strained four-membered rings, even though this type of coordination has been tentatively proposed for an intermediate observed in the solutions of [RhCl(CO)(PPhpy₂)] [1]. A bridging PPhpy₂ would be equally consistent with the experimental evidence. The strain is released if the coordination adopted is **B**, where the bridging nature of PPhpy₂ must necessarily give rise to polymers or cyclic oligomers. Unfortunately, the low stability of the compound in solution in the conditions used for molecular weight determination (increasing decomposition is observed as a function of the time in solution) precludes precise measurements. Even so, the values obtained in several determinations, ranging from 565 (*n* = 1.3, for samples with high decomposition) to 1670 (*n* = 3.8, for the best preserved sample) point to a rather small oligomer (perhaps *n* = 4) splitting into smaller fragments which severely reduce the apparent molecular weight as decomposition progresses. The solubility of the compound in some solvents is also consistent with a low degree of polymerization.

From the reactions reported above, it can be concluded that PPhpy₂ gives more stable molybdenum(0)

complexes when it coordinates as *P*-donor (1 or 2), than when it acts as *N,N'*-donor (as in 3). It was of interest to determine the behaviour of the ligand toward harder metal centres, such as molybdenum(II).

The addition of an equimolar amount of iodine to 4 in CH_2Cl_2 at 0°C , leads immediately to $[\text{MoI}_2(\text{CO})_3(\text{py}_2\text{PhP-}N,N')]$, 5, which was isolated in *ca.* 80% yield ((vii), Scheme 1). The molar conductivity of 5 is very low, as expected for a non-electrolyte, and C,H,N analyses agree with the proposed stoichiometry. The spectroscopic data clearly indicate the coordination of the phosphine as a chelating *N,N'*-donor. The pattern in the stretching C–O region of the IR spectrum (Table 1) is very similar to those of complexes $[\text{MX}_2(\text{CO})_3(\text{bipy})]$ ($\text{M} = \text{Mo}$ or W ; $\text{X} = \text{Br}$ or I) [8]. The chemical shift of the singlet in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (Table 1) appears in the same region as that of the free donor, consistent with the noncoordination of the phosphorus atom. In the ^1H NMR spectrum, the H^6 protons give rise to two different resonances, one of them at δ 9.47 ppm (see Experimental). This deshielding effect has been found in palladium(II) complexes when a halo-ligand is *cis* with respect to a nitrogen atom [11]. It seems that this also applies to a seven-coordinated complex 5.

The formation of 5 in this reaction shows the preference of molybdenum(II) for the pyridine moiety. The oxidation of the metal during the reaction leads not only to noncoordination of the phosphorus atom, but also to stronger Mo–N bonds since, in contrast to the molybdenum(0) complex 3, 5 is fairly stable in solution. Compound 5 can also be synthesized by replacing weak ligands by PPhpy_2 in the appropriate molybdenum(II) substrate. Thus, the reaction of equimolar amounts of PPhpy_2 and $[\text{MoI}_2(\text{CO})_3(\text{NCMe})_2]$ affords 5 ((ix), Scheme 1), in similar conditions and yield as before.

Similarly $[\text{MoBr}(\eta^3\text{-CH}_2\text{CHCH}_2)(\text{CO})_2(\text{py}_2\text{PhP-}N,N')]$, 6, is obtained by oxidative addition of allylbromide to 4 ((viii), Scheme 1), although this time heating under reflux in chloroform was needed to eliminate a molecule of carbon monoxide. Alternatively, addition of an equimolar amount of PPhpy_2 to $[\text{MoBr}(\eta^3\text{-CH}_2\text{CHCH}_2)(\text{CO})_2(\text{NCMe})_2]$, in CH_2Cl_2 at r.t., causes the substitution of the acetonitrile ligands by PPhpy_2 , acting as a chelating *N,N'*-donor ((x), Scheme 1). IR spectra, molar conductivity (non-conductor), and C,H,N analyses also support the proposed structure. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 6 again shows one singlet characteristic of uncoordinated phosphorus (Table 1), and signals due to a trihapto allyl group and PPhpy_2 are observed in the ^1H NMR spectrum (see Experimental section). In this case, both H^6 are equivalent and give rise to a broad doublet.

In summary, the results agree with the HSAB prin-

ciple, as soft molybdenum(0) centres show preference for *P*-coordination, whereas hard molybdenum(II) centres stabilize *N,N'*-chelation.

3. Experimental details

All reactions were carried out under an atmosphere of dry nitrogen. Solvents were distilled according to standard procedures [12], and purged with dinitrogen prior to use. $[\text{Mo}(\text{CO})_6]$ and $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$ were purchased from Aldrich, and the latter was sublimed *in vacuo* to obtain anhydrous Me_3NO . $[\text{Mo}(\text{CO})_4(\text{NBD})]$ [13], $[\text{MoI}_2(\text{CO})_3(\text{NCMe})_2]$ [14], and $[\text{MoBr}(\eta^3\text{-CH}_2\text{CHCH}_2)(\text{CO})_2(\text{NCMe})_2]$ [15] were prepared according to literature procedures, whereas PPhpy_2 was synthesized [5] as reported for Ppy_3 [16], but starting from PPhCl_2 .

The progress of the reactions was monitored by solution IR spectra in the $2100\text{--}1700\text{ cm}^{-1}$ region. Filtrations were carried out on dry Celite without exclusion of air. IR spectra were obtained using a Perkin-Elmer 833 apparatus, in NaCl windows for solutions or as Nujol emulsions. NMR spectra were recorded on Bruker AC80 or AC300 instruments, at r.t. The mass spectrum of compound 3 was obtained using a Hewlett-Packard 5987A mass spectrometer operating at 70 eV. Masses were correlated with the following isotopes: ^1H , ^{12}C , ^{14}N , ^{16}O , ^{31}P , and ^{98}Mo . Electrical conductivity measurements were carried out at r.t. with a Crison 522 conductivimeter using 5×10^{-4} M nitromethane solutions. Molecular weights were measured in a Knauer Vapor Pressure Osmometer using chloroform solutions, and elemental analyses were performed on a Perkin-Elmer 2400B microanalyzer. Solution IR bands in the carbonyl region, $^{31}\text{P}\{^1\text{H}\}$ NMR data, and C,H,N microanalyses for the compounds are given in Table 1.

3.1. Synthesis of $[\text{Mo}(\text{CO})_5(\text{PPhpy}_2\text{-P})]$, 1

A 100 ml Schlenk flask was charged with 0.528 g (2.0 mmol) of $\text{Mo}(\text{CO})_6$, and 20 ml of MeCN. A solution of 0.150 g (2.0 mmol) of Me_3NO in 10 ml of MeCN was then added dropwise to the stirred mixture at r.t. Once the addition had been completed, the solvent was removed *in vacuo*. The yellowish residue was dissolved in 25 ml of CH_2Cl_2 , 0.529 g (2.0 mmol) of PPhpy_2 were added as a solid, and the solution was stirred at r.t. for 2 h. The solution was filtered, and 15 ml of hexane were added to the filtrate. Concentration of this solution *in vacuo* to *ca.* 2 ml gave a pale yellow microcrystalline solid. The mother liquors were syringed off, and the solid was washed with cold (*ca.* -20°C) hexane (2×2 ml), and dried *in vacuo*, yielding 0.745 g (1.49

mmol, 74%) of **1**. IR (Nujol, cm^{-1}): 3040vw, 2073s, 2018vw, 1991m, 1937vsbr, 1573w, 1564vw, 1481vw, 1455m, 1437w, 1425m, 1282vw, 1158vw, 1097vw, 1048vw, 988w, 770w, 750w, 743w, 720vw, 696m, 667vw, 606m, 585m. $^1\text{H NMR}$ (300 MHz, CD_2Cl_2): δ 8.80 (d, J 4.0 Hz, 2H), 7.7–7.3 (m, 11H).

3.2. Synthesis of $[\text{Mo}(\text{CO})_4(\text{PPhy}_2\text{-P})_2]$, **2**

0.290 g (1.1 mmol) of PPhy_2 were added to a solution of 0.150 g (0.5 mmol) of $[\text{Mo}(\text{CO})_4(\text{NBD})]$ in 25 ml of toluene. The mixture was stirred at r.t. during 3 h, during which time an off-white solid precipitated. The solid was filtered off, washed with Et_2O (3×5 ml), and dried, yielding 0.262 g (0.36 mmol, 71%) of **2**. IR (Nujol, cm^{-1}): 3050vw, 2018m, 1905vsbr, 1869s, 1838m, 1573w, 1564vw, 1451m, 1437w, 1424w, 1158vw, 1094w, 1048vw, 989vw, 771w, 751w, 742w, 722vw, 699w, 666w. $^1\text{H NMR}$ (300 MHz, CD_2Cl_2): δ 8.50 (d, J 4.6 Hz, 4H), 7.6–7.1 (m, 22H).

3.3. Synthesis of $[\text{Mo}(\text{CO})_4(\text{py}_2\text{PhP-N,N}')]_3$, **3**

0.132 g (0.5 mmol) of PPhy_2 were added to a solution of 0.150 g (0.5 mmol) of $[\text{Mo}(\text{CO})_4(\text{NBD})]$ in 25 ml of CH_2Cl_2 . The solution was stirred at r.t. for 12 h, during which it changed from yellow to dark red. The solvent was removed *in vacuo*, and the dark residue was dissolved in 25 ml of toluene, and immediately filtered (to remove **2**). The solvent of the filtrate was quickly removed *in vacuo*, and crystallization of the dark residue from CH_2Cl_2 /hexane at -20°C yielded 0.074 g (0.16 mmol, 31%) of **3** as dark red crystals. IR (Nujol, cm^{-1}): 3040 vw, 3025vw, 2010s, 1889vs, 1877vs, 1817vs, 1587w, 1574w, 1425w, 1275m, 1229vw, 1163m, 1096m, 1061m, 989vw, 890vw, 766m, 752m, 739w, 730m, 699m, 667vw, 648w, 639vw, 607w, 584m. $^1\text{H NMR}$ (80 MHz, CDCl_3): δ 9.21 (dq, J 5.5 and 0.8 Hz, 2H), 7.9–7.0 (m, 11H). Mass spectrum (EI), m/z (relative intensity): 446 (M^+-CO , 7), 390 ($\text{MoPPhy}_2\text{-CO}^+$, 6), 362 (MoPPhy_2^+ , 30), 283 (MoPPhy^+-H , 29), 264 (PPhy_2^+ , 17), 185 (PPhy^+-H , 100), 180 ($\text{Ph}_2\text{C}_2\text{H}_2^+$, 14), 157 (py_2^++H , 11), 154 (Ph_2^+ , 16), 107 ($\text{C}_6\text{H}_5\text{NO}^+$, 28), 98 (Mo^+ , 14), 79 ($\text{C}_5\text{H}_5\text{N}^+$, 21), 78 (C_6H_6^+ , 50), 77 ($\text{C}_6\text{H}_6^+-\text{H}$, 14).

3.4. Syntheses of $\{\text{Mo}(\text{CO})_3(\mu\text{-PPhy}_2)\}_n$, **4**

A mixture of 0.264 g (1.0 mmol) of $[\text{Mo}(\text{CO})_6]$, 0.264 g (1.0 mmol) of PPhy_2 , and 30 ml of toluene was heated under reflux for 2 h, during which time a yellow-orange solid precipitated. The mixture was allowed to cool to r.t., and the solid was filtered off, and washed with hexane (3×5 ml), and dried, yielding 0.347 g (0.78 mmol, 78%) of **4**. IR (Nujol, cm^{-1}): 3060vw, 1923vs, 1824s, 1783vs, 1585w, 1569vw, 1416w, 1229w, 1189vw, 1165m, 1094w, 1060w, 759m, 743w,

722vw, 694w, 655vw. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 9.00 (d, J 5.2 Hz, 2H), 7.43 (t, J 6.4 Hz, 1H), 7.3–7.1 (m, 6H), 6.93 (t, J 7.4 Hz, 2H), 6.75 (t, J 6.2 Hz, 2H).

When compounds **1**, **2**, or **3** were heated under reflux in toluene, **4** was obtained in 72%, 57% and 63% yields, respectively, after work-up as before.

3.5. Syntheses of $[\text{MoI}_2(\text{CO})_3(\text{py}_2\text{PhP-N,N}')]_3$, **5**

Method A: 0.056 g (0.22 mmol) of iodine were added to a mixture containing 0.089 g (0.2 mequiv) of **4**, and 10 ml of CH_2Cl_2 , at 0°C . Once the iodine had dissolved, 10 ml of EtOH were added. Concentration of the solution *in vacuo* to ca. 2 ml gave an orange microcrystalline solid. The mother liquors were syringed off, and the solid was washed with Et_2O (3×3 ml), and dried *in vacuo*, yielding 0.113 g (0.16 mmol, 81%) of **5**. Method B: a solution of 0.253 g (0.5 mmol) of $\text{MoI}_2(\text{CO})_3(\text{NCMe})_2$ and 0.132 g (0.5 mmol) of PPhy_2 in 20 ml of CH_2Cl_2 was stirred at r.t. for 5 min, and then 10 ml of EtOH were added. Work-up as before gave 0.275 g (0.39 mmol, 79%) of **5**. IR (Nujol, cm^{-1}): 3072vw, 3052vw, 2030vs, 1972vs, 1929vs, 1590w, 1573w, 1564w, 1441m, 1421m, 1191vw, 1161vw, 1140w, 1105vw, 1090w, 1048w, 1022w, 989w, 777m, 766w, 744m, 688w. $^1\text{H NMR}$ (80 MHz, CDCl_3): δ 9.47 (br, J ca. 5 Hz, 1H), 8.76 (br, J ca. 5 Hz, 1H), 7.9–7.3 (m, 11H). Conductivity (MeNO_2): 20 $\text{S cm}^2 \text{mol}^{-1}$.

3.6. Syntheses of $[\text{MoBr}(\eta^3\text{-CH}_2\text{CHCH}_2)(\text{CO})_2(\text{py}_2\text{PhP-N,N}')]_3$, **6**

Method A: a mixture of 0.089 g (0.2 mequiv) of **4**, 20 ml of CHCl_3 and 0.2 ml (2.3 mmol) of allylbromide was heated under reflux during 2 h. The volatiles were removed *in vacuo*, and the dark yellow residue was dissolved in 10 ml of CH_2Cl_2 , and filtered. Addition of 10 ml of EtOH to the filtrate, and concentration *in vacuo* to ca. 2 ml gave a yellow microcrystalline solid. The mother liquors were syringed off, and the solid was washed with Et_2O (3×3 ml), and dried *in vacuo*, yielding 0.066 g (0.12 mmol, 61%) of **6**. Method B: a solution of 0.071 g (0.2 mmol) of $[\text{MoBr}(\eta^3\text{-CH}_2\text{CHCH}_2)(\text{CO})_2(\text{NCMe})_2]$, and 0.053 g (0.2 mmol) of PPhy_2 in 10 ml of CH_2Cl_2 was stirred at r.t. for 5 min, and then 10 ml of EtOH were added. Work-up as before gave 0.071 g (0.13 mmol, 66%) of **6**. IR (Nujol, cm^{-1}): 3065vw, 3046vw, 1939vs, 1824vs, 1585m, 1562vw, 1462w, 1454w, 1420w, 1402vw, 1315vw, 1276w, 1228vw, 1163vw, 1094w, 1066w, 1047w, 1010vw, 998vw, 894vw, 875vw, 853vw, 804vw, 775m, 764w, 754m, 737m, 700m. $^1\text{H NMR}$ (80 MHz, CDCl_3): δ 9.44 (d, J 5.6 Hz, 2H), 7.7–7.0 (m, 11H), 4.16 (m, 1H, CH_2CHCH_2), 3.45 (br, 2H, CH_2CHCH_2 syn), 1.54 (d, J 9.3 Hz, 2H, CH_2CHCH_2 anti). Conductivity (MeNO_2): 5.4 $\text{S cm}^2 \text{mol}^{-1}$.

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