Synthesis and Characterization of Carbonyl Group-6-Metal Derivatives with Ligand *N*,*N*-Bis(diphenylphosphino)naphthalen-1-amine (= *N*-(Diphenylphosphino)-*N*-naphthalen-1-yl-*P*,*P*-diphenylphosphinous Amide). Molecular Structure of *cis*-Tetracarbonyl[*N*-(diphenylphosphino-κ*P*)-*N*-naphthalen-1-yl-*P*,*P*-diphenylphosphinous amide-κ*P*]molybdenum (*cis*-[$Mo(CO)_4\{C_{10}H_7$-1-$N(PPh_2)_2\}$])

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The reaction of *N*,*N*-bis(diphenylphosphino)naphthalen-1-amine (**1**) with $[M(CO)_6]$ (M = Cr, Mo, W; 1:1 molar ratio) afforded *cis*-$[M(CO)_4(\mathbf{1})]$ **2** (M = Cr), **3** (M = Mo), and **4** (M = W). Compounds **2** – **4** were identified and characterized by elemental analysis and multinuclear NMR (^{1}H-, ^{13}C-, and ^{31}P-NMR) and IR spectroscopy. A crystal-structure determination of complex **3** was carried out.

Introduction. – In an extension of our interest and the interest of others [1] on the synthesis and solid-state structures of phosphorus(III) ligands containing direct P–N bonds and their derivatives [2][3], as these are interesting in the field of medicinal [4 – 7] and catalytic chemistry [8 – 10], as well as herbicidal, neuroactive, and antimicrobial agents [11 – 13], we herein report the synthesis and spectroscopic properties of group-6-metal carbonyl complexes **2** – **4** and the crystal structure of **3**.

Experimental. – *General.* All experiments were carried out under purified dry N_2 by using standard *Schlenk* and vacuum-line techniques. Solvents were dried and freshly distilled under N_2 [14]. The chemicals $[M(CO)_6]$ (M = Cr, Mo, and W) were used as purchased. *N*,*N*-Bis(diphenylphosphino)naphthalen-1-amine (= *N*-(diphenylphosphino)-*N*-napthalen-1-yl-*P*,*P*-diphenylphosphinous amide; **1**) was prepared according to the method described previously [3]. M.p.: *Gallenkamp* apparatus; open capillaries. IR spectra: *Perkin-Elmer-2000* FT-IR spectrometer; range 4000 – 400 cm^{-1}; KBr disks; in cm^{-1}. NMR Spectra: *Bruker-Avance-DRX-400* spectrometer; at 400.17 (^{1}H), 100.63 (^{13}C), and 161.98 MHz (^{31}P) and 25°; $SiMe_4$ for ^{1}H and 85% H_3PO_4 for ^{31}P as external standards; δ in ppm. Microanalyses: *Flash-2000* elemental analyzer.

cis-*[*N,*N*-*Bis(diphenylphosino-*κP*)*naphthalen-1-amine*]tertracarbonylchromium(0)* (=cis-*Tetracarbonyl[*N-*(diphenylphosphino-*κP*)*-N-*naphthalen-1-yl-*P,P-*diphenylphosphinous amide-*κP*]chromium*; **2**). Ligand **1** (2.00 g, 3.91 mmol) was added to a soln. of $[Cr(CO)_6]$ (0.86 g, 3.91 mmol) in toluene (80 ml), and the mixture was heated under reflux for 36 h. The soln. was filtered, the solvent evaporated, and the dark yellow solid recrystallized from CH_2Cl_2/hexane 1:1 (*v*/*v*) at 25°: **2** (70%). Yellow crystals. M.p. 180 – 183°. IR (selected bands): 1888*s* (br.), 1918*s*, 2006*s* (C≡O). ^{1}H-NMR ($CDCl_3$): 6.40 – 7.72 (*m*, $C_{10}H_7$, 4 Ph). ^{13}C-NMR ($CDCl_3$): 124.80, 125.17, 125.61, 125.94, 127.09, 127.92, 128.61, 129.59, 130.46, 131.32, 132.56, 134.07, 135.44, 138.75 ($C_{10}H_7$ and 4 Ph); 221.24 ($C{\equiv}O_{eq}$); 228.17 ($C{\equiv}O_{ax}$). ^{31}P-NMR ($CDCl_3$): 117.41 (*s*, 2 P). Anal. calcd. for $C_{38}H_{27}CrNO_4P_2$: C 67.56, H 4.03, N 2.07; found: C 67.58, H 4.05, N 2.04.

cis-*[*N,N-*Bis(diphenylphosino-*κP*)naphthalen-1-amine]tertracarbonylmolybdenum(0)* (=cis-*Tetracarbonyl[*N-*(diphenylphosphino-*κP*)-N-naphthalen-1-yl-*P,P-*diphenylphosphinous amide-*κP*]molybdenum*; **3**). A mixture of ligand **1** (0.40 g, 0.76 mmol) and $[Mo(CO)_6]$ (0.20 g, 0.76 mmol) in benzene (40 ml) was refluxed for 12 h (→ dark brown soln.). The solvent was evaporated, the product extracted into hexane (40 ml), and the extract cooled to 4°: **3** (80%). Yellow crystals. M.p. 235–238°. IR (selected bands): 1907*s* (br.), 1924*s*, 2023*s* (C≡O). ^{1}H-NMR ($CDCl_3$): 6.42–7.68 (*m*, $C_{10}H_7$ and 4 Ph). ^{13}C-NMR ($CDCl_3$): 124.69, 125.19, 125.51, 126.98, 127.21, 127.51, 128.23, 128.60, 130.17, 130.92, 131.37, 132.51, 133.92, 139.56 ($C_{10}H_7$, 4 Ph); 212.37 (C≡O_{eq}); 218.37 (C≡O_{ax}). ^{31}P-NMR ($CDCl_3$): 93.43 (s, 2 P). Anal. calc. for $C_{38}H_{27}MoNO_4P_2$: C 63.43, H 3.78, N 1.95; found: C 63.40, H 3.73, N 1.93.

cis-*[*N,N-*Bis(diphenylphosino-*κP*)naphthalen-1-amine]tetracarbonyltungsten(0)* (=cis-*Tetracarbonyl[*N-*(diphenylphosphino-*κP*)-N-naphthalen-1-yl-*P,P-*diphenylphosphinous amide-*κP*]tungsten*; **4**). As described for **2**, with $[W(CO)_6]$ (1.38 g, 3.91 mmol) instead of $[Cr(CO)_6]$: **4** (60%). Light yellow solid. M.p. 160–163°. IR (selected bands): 1889*s* (br.), 1910*s*, 2016*s* (C≡O). ^{1}H-NMR ($CDCl_3$): 6.42–7.72 (*m*, 27 H, $C_{10}H_7$, 4 Ph). ^{13}C-NMR ($CDCl_3$): 124.52, 125.13, 125.98, 126.70, 127.12, 127.30, 128.10, 128.58, 130.16, 130.91, 131.34, 132.44, 133.91, 139.54 ($C_{10}H_7$, 4 Ph); 203.60 (C≡O_{eq}); 210.65 (C≡O_{ax}). ^{31}P-NMR ($CDCl_3$): 70.19 (s, 2 P). Anal. calc. for $C_{38}H_{27}NO_4P_2W$: C 56.53, H 3.37, N 1.73; found: C 56.52, H 3.38, N 1.75.

Data Collection and Structure Determination of **3**. Crystallographic data are given in *Table 1*. Data were collected with a *Bruker-AXS-Smart-Apex-CCD* diffractometer; $\lambda(Cu_{K\alpha}) = 1.54178$ Å. All observed reflections were used for the determination of the unit-cell parameters. Indexing was performed with SMART [15]. Frames were integrated with the SAINT software package [16]. Absorption correction was performed by the multi-scan method implemented in SADABS [17]. Crystal structures were solved by using SHELXS-97 and refined by using SHELXL-97 contained in the SHELXTL and WinGX-1.70.01 program packages [18]. All non-H-atoms were refined with anisotropic displacement parameters. All H-atoms bonded to C-atoms were placed in geometrically optimized positions and refined with an isotropic displacement parameter relative to the attached atoms. CCDC-876277 conatins the supplementary crystallographic data (excluding structure factors) for the structure of **3**. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/data_request/cif.

Table 1. *Crystal Data and Structure Refinement of* **3**

Formula	$C_{38}H_{27}MoNO_4P_2$	Z	4
M_r	719.49	ρ_{calcd} [Mg m^{-3}]	1.473
Temp. [K]	100	$F(000)$	1464
Crystal system	triclinic	Abs. coeff. [mm^{-1}]	4.584
Space group	*P*-1	No. of refl. collected	13393
a [Å]	11.1442(5)	No. of independant refl.	8045
b [Å]	16.7516(6)	R_{int}	0.0304
c [Å]	17.5177(7)	No. of parameters	829
α [°]	89.392(2)	R_1 ($I > 2\sigma(I)$)	0.0356
β [°]	82.816(3)	wR_2 (all data)	0.0890
γ [°]	89.927(3)	$\Delta\rho_{max}$ [e·Å^{-3}]	0.524
V [Å^3]	3244.4(2)	$\Delta\rho_{min}$ [e·Å^{-3}]	−0.698

Results and Discussion. – *Synthesis.* The *Scheme* summarizes the synthesis of **2**–**4**. The reaction of ligand **1** with 1 equiv. of $[M(CO)_6]$ (M = Cr, or Mo) under reflux in toluene afforded *cis*-$[Cr(CO)_4(\mathbf{1})]$ (**2**) and *cis*-$[W(CO)_4(\mathbf{1})]$ (**4**), respectively. Moreover, reaction of ligand **1** with 1 equiv. of $[Mo(CO)_6]$ under reflux in benzene gave *cis*-$[Mo(CO)_4(\mathbf{1})]$ (**3**). Compounds **2**–**4** are moderately stable to air and moisture.

Scheme. *Preparation of* **2**–**4**

1

2 M = Cr
3 M = Mo
4 M = W

Compounds **2**–**4** were isolated from the reaction solution and fully characterized by elemental analysis, IR and multinuclear NMR spectroscopy. Furthermore, the molecular structure of **3** was elucidated by single crystal X-ray diffraction.

^{1}H-, ^{13}C-, and ^{31}P-NMR Spectra. Due to the presence of naphthalenyl and phenyl groups and coupling with ^{31}P, the aromatic region in the ^{1}H-, and ^{13}C-NMR spectra of **2**–**4** was complex and difficult to fully interpret [19]. The ^{1}H-NMR spectra of **2**–**4** had the expected pattern characteristic for the organic ligand **1**; the resonances corresponding to the phenyl and naphthalenyl protons displayed overlapped *m* in the region δ(H) 6.40–7.72.

The ^{13}C-NMR spectra of the carbonyl ligands of **2**–**4** showed two signals due to the carbonyl ligands oriented *trans* and *cis* to the P-atoms. The δ(C) of the carbonyl ligands decreased in the order of Cr > Mo > W coordination, in parallel with the increasing number of electrons in the central metal atom [20].

The ^{31}P-NMR signals of **2**–**4** appeared as *s* signals at δ(P) 117.41 (**2**), 93.43 (**3**), and 70.19 (**4**), indicating two equivalent P-atoms. The δ(P) increased upon coordination of ligand **1** (δ(P) 63.46) with the metal center, the shift being *ca.* 54 ppm for **2**, *ca.* 30 ppm of **3** and *ca.* 7 ppm for **4**, and the δ(P) decreased in the order of Cr > Mo > W coordination, in agreement with the observation that such a δ(P) should decrease as one descends in a given periodic group [21].

IR Spectra and Yields. The IR spectra of **2**–**4** showed bands in the range 1888–2023 cm^{-1} due to the $\tilde{\nu}$(C≡O) stretching typical for *cis*-[M(CO)$_4$L$_2$] complexes [22]. The carbonyl frequencies of the complexes **2**–**4** were very near those of closely related complexes with ligands in which the P-atom is bonded to C-atoms only. The absence of any marked effect shows that the replacement of CH or CHR by NR does not greatly change the ability of the P-atoms to accept electrons from the metal [23]. Complexes **2**–**4** were obtained in 60–80% yield.

Molecular Structure of **3**. Crystals of **3** were obtained as described in the *Exper. Part*. Complex **3** crystallized in the triclinic space group $P\bar{1}$. Selected interatomic distances and angles are collected in *Table 2*, and the molecular structure is depicted in the *Figure*.

The X-ray structure of **3** contains two crystallographically independent molecules, **3a** and **3b** (*Fig.*), in the asymmetric unit. These differ in the orientation of the naphthalenyl group. The crystal structure of **3** shows a distorted octahedral environment around the Mo-atom surrounded by four terminal CO ligands and two P-centers.

Table 2. *Selected Bond Lengths* [Å] *and Bond Angles* [°] *of* **3a** *and* **3b**

3a		**3b**	
Mo1–C(1)	2.039(5)	Mo2–C(39)	2.048(5)
Mo(1)–C(2)	1.990(4)	Mo(2)–C(40)	2.001(4)
Mo(1)–C(3)	2.001(5)	Mo(2)–C(41)	2.016(5)
Mo(1)–C(4)	2.034(5)	Mo(2)–C(42)	2.020(5)
Mo(1)–P(1)	2.5036(9)	Mo(2)–P(3)	2.4755(10)
Mo(1)–P(2)	2.4925(10)	Mo(2)–P(4)	2.4898(9)
P(1)–N(1)	1.723(3)	P(3)–N(2)	1.715(3)
P(2)–N(1)	1.710(3)	P(4)–N(2)	1.725(3)
P(1)–C(23)	1.817(4)	P(3)–C(43)	1.830(4)
P(1)–C(17)	1.832(4)	P(3)–C(49)	1.818(4)
P(2)–C(11)	1.822(4)	P(4)–C(65)	1.814(4)
P(2)–C(5)	1.825(4)	P(4)–C(71)	1.829(4)
N(1)–C(29)	1.459(4)	N(2)–C(55)	1.446(4)
Σ angles at N(1)	359.93	Σ angles at N(2)	359.93
P(1)–Mo(1)–P(2)	65.94(3)	P(3)–Mo(2)–P(4)	66.14(3)
P(1)–Mo(1)–C(1)	91.96(10)	P(3)–Mo(2)–C(39)	92.19(11)
P(1)–Mo(1)–C(2)	165.15(12)	P(3)–Mo(2)–C(40)	98.82(12)
P(1)–Mo(1)–C(3)	98.63(10)	P(3)–Mo(2)–C(41)	165.76(11)
P(1)–Mo(1)–C(4)	93.18(10)	P(3)–Mo(2)–C(42)	87.55(11)
P(2)–Mo(1)–C(1)	92.77(12)	P(4)–Mo(2)–C(39)	89.96(9)
P(2)–Mo(1)–C(2)	99.23(12)	P(4)–Mo(2)–C(40)	164.87(12)
P(2)–Mo(1)–C(3)	164.46(11)	P(4)–Mo(2)–C(41)	100.00(10)
P(2)–Mo(1)–C(4)	93.39(11)	P(4)–Mo(2)–C(42)	91.41(10)
P(1)–N(1)–P(2)	104.73(16)	P(2)–N(2)–P(4)	103.93(15)
N(1)–P(1)–Mo1	93.62(10)	N(2)–P(3)–Mo2	94.70(11)
N(1)–P(2)–Mo1	94.32(11)	N(2)–P(4)–Mo2	93.94(10)
N(1)–P(1)–C(17)	103.61(16)	N(2)–P(3)–C(43)	107.76(16)
N(1)–P(1)–C(23)	106.24(16)	N(2)–P(3)–C(49)	109.09(15)
N(1)–P(2)–C(5)	108.39(16)	N(2)–P(4)–C(65)	107.42(16)
N(1)–P(2)–C(11)	107.06(16)	N(2)–P(4)–C(71)	107.81(17)
C(17)–P(1)–C(23)	104.72(17)	C(43)–P(3)–C(49)	100.38(17)
C(5)–P(2)–C(11)	101.62(18)	C(65)–P(4)–C(71)	102.22(17)
P(2)–Mo(1)–P(1)–N(1)	7.6(1)	P(3)–Mo(2)–P(4)–N(2)	7.4(1)

The ability of compound **1** to act as a bidentate *P,P′*-chelating ligand to the Mo-atom results in the formation of a four-membered metallacycle, *i.e.*, P–Mo–P–N, that is nearly planar with a torsion angle P–Mo–P–N of 7.6(1)° in **3a** and 7.4(1)° in **3b** with a smaller P–Mo–P bite angle (65.94(3)° (**3a**) and 66.14(3)° (**3b**)) and larger P–N–P bond angle (104.73(16)° (**3a**) and 103.93(15)° (**3b**)).

A comparison of the P–Mo–P and P–N–P bond angles of **3a** and **3b** (*Table 2*) with those of the four-membered ring of the similar *cis*-chelated tetracarbonylmolybdenum(0) complexes **5**–**9**, tetracarbonylchromium(0) complexes **10**–**12**, and tetracarbonyltungsten(0) complexes **13** and **14** (*Table 3*) showed that the P–Mo–P bite angles in **3a** and **3b** are slightly larger than those in **5**–**9**, **13**, and **14** and smaller than those in **10**–**12**. The P–N–P bond angles in **3a** and **3b** are larger than those in **5**–**8**, **10**–**12**, and **13** and smaller than those in **9** and **14**. The P–M–P bite angles in *cis*-chelated tetracarbonylchromium(0) complexes **10**–**12** are in average 67.98°, being about 2°

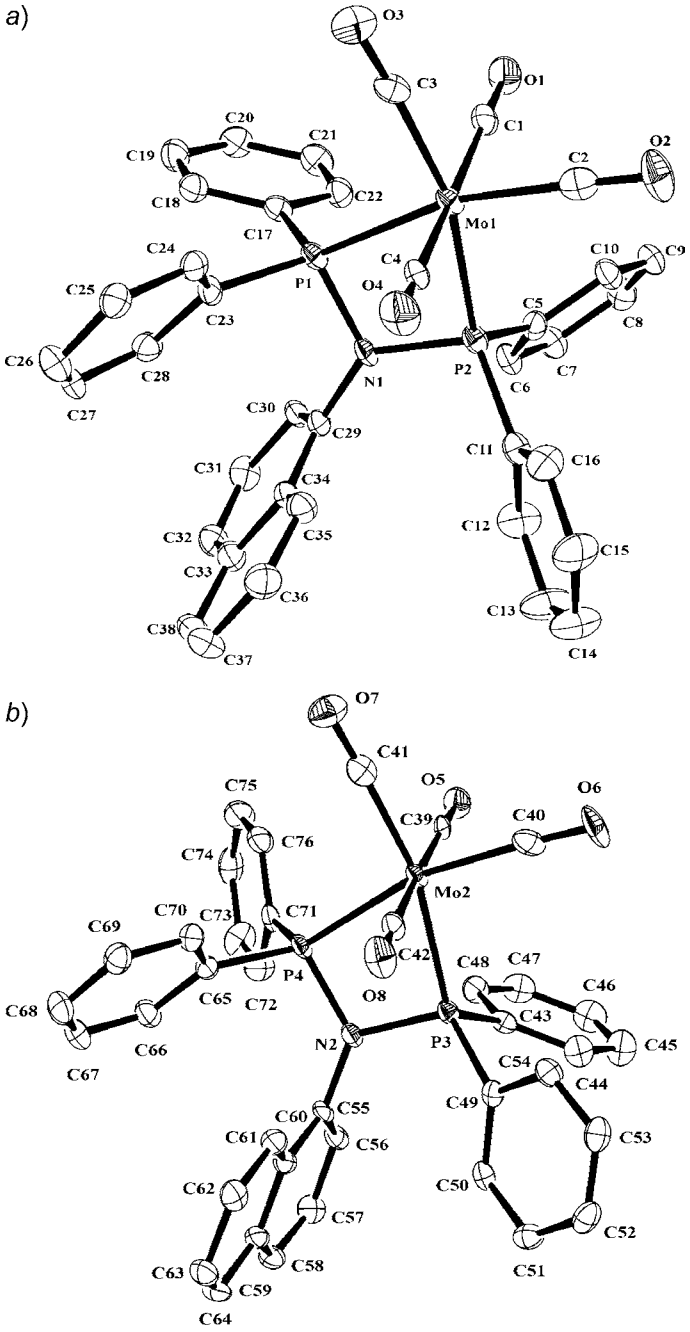

Figure. *Molecular structure of the two independent molecules* a) **3a** *and* b) **3b**. H-Atoms are omitted for clarity.

Table 3. *Selected Tetracarbonyl(Group-6-Metal) Complexes with Phosphinoamine Ligands*

Complex	No.	Ring syst.	N–P (av.) [Å][a])	M–P (av.) [Å][a])	P–M–P [°]	P–N–P [°]	Ref.
cis-[Mo(CO)$_4${(P(OC$_6$H$_4$OMe-*o*)$_2$)$_2$NPh}]	**5**	4	1.687	2.499	65.02(4)	102.40(2)	[24]
cis-[1,4-(Mo(CO)$_4$)$_2${(Ph$_2$P)$_2$NCH$_2$)$_2$C$_6$H$_4$}]	**6**	4	1.713	2.506	65.14(1)	103.39(9)	[25]
cis-[Mo(CO)$_4${PhN(P(OC$_6$H$_3$(OMe-*o*)(C$_3$H$_5$-*p*))$_2$)$_2$}]	**7**	4	1.709	2.439	65.29(2)	100.70(11)	[26]
cis-[Mo(CO)$_4${(Ph$_2$P)$_2$N(*o*-C$_6$H$_4$OMe)}]	**8**	4	1.729	2.499	65.78(2)	103.43(8)	[27]
cis-[Mo(CO)$_4${(Ph$_2$P)$_2$NH}]·MeCN	**9**	4	1.685	2.498	65.29(6)	106.20(2)	[28]
cis-[Cr(CO)$_4${((*o*-MeOC$_6$H$_4$)$_2$P)$_2$NMe}]	**10**	4	1.699	2.364	67.54(2)	101.24(7)	[29]
cis-[Cr(CO)$_4${(Ph$_2$P)$_2$N^{i}Pr}]	**11**	4	1.713	2.350	67.82(4)	99.86(11)	[30]
cis-[Cr(CO)$_4${(Ph$_2$P)$_2$NH}]	**12**	4	1.692	2.354	68.58(2)	103.24(9)	[31]
cis-[W(CO)$_4${PhN(P(OC$_6$H$_3$(OMe-*o*)(C$_3$H$_5$-*p*))$_2$)$_2$}]	**13**	4	1.709	2.433	65.40(2)	100.52(13)	[26]
cis-[W(CO)$_4${(Ph$_2$P)$_2$NH}]	**14**	4	1.673	2.492	64.70(2)	105.70(9)	[31]
cis-[Mo(CO)$_4${PPh$_2$NH$_2$}$_2$]	**15**	–	1.680	2.526	90.06(2)	–	[32]
cis-[Mo(CO)$_4${PPh$_2$NH^{t}Bu}$_2$]	**16**	–	1.665	2.545	95.44(3)	–	[33]
trans-[Mo(CO)$_4${PPh$_2$N(H)C$_6$H$_{11}$}$_2$]	**17**	–	1.679	2.046	180.0	–	[34]
cis-[Mo(CO)$_4${MeC$_6$H$_3$(PNHPPh$_2$)$_2$-3,4}]	**18**	7	1.703	2.494	84.6(1)	–	[35]

[a]) av. = averaged.

wider than the average value in the *cis*-chelated tetracarbonylmolybdenum(0) complexes **3a** and **3b** (averaged 66.04°).

The P–Mo–P bite angles in **3a** and **3b** are relatively close to each other and significantly lower than the ideal 90° in a regular square-planar geometry. Apparently, the presence of the naphthalenyl and phenyl groups decreases the P–Mo–P bite angle, presumably as a result of steric reasons, as the relatively bulky naphthalenyl and phenyl groups occupy much of the lateral space surrounding the P–Mo–P–N ring, which leads to distorted square-planar coordination geometry around the Mo-atom with the phosphinoamine moieties coordinated in a mutual *cis*-fashion, in agreement with the spectroscopic data. The P–N–P bond angles (104.73(16)° (**3a**) and 103.93(15)° (**3b**)) are significantly smaller than those in the free diphosphinoamine ligands [24][36] due to the formation of a strained four-membered chelate ring.

The napthalenyl moietes in **3a** and **3b** are almost planar and virtually perpendicular to the P–Mo–P–N planes. A planar environment would be expected for the three-coordinate N-atoms in **3a** and **3b**, and the sums of bond angles in **3a** and **3b** are indeed close to 360° (*Table 2*).

The P–Mo–C(*trans*) angles of **3a** (164.46(11)° and 165.15(12)°) and **3b** (164.87(12)° and 165.76(11)°) differ significantly from 180°. The variations of the *trans* angles (0.69 (**3a**) and 0.89° (**3b**)) are smaller than those of **5** (162.39(13)° *vs.* 165.83(15)°), **6** (162.74(7)° *vs.* 164.62(7)°), and **9** (164.70(1) *vs.* 169.00(1)°).

The average P–N bond distances in **3a** (1.717 Å) and **3b** (1.720 Å) are essentially the same and within the expected value range in comparison to the similar *cis*-chelated tetracarbonyl complexes **5**–**14** (*Table 3*), but they are shorter than the sum of the *Pauling* covalent radii (1.77 Å), as expected due to P–N π-bonding. Consistent with this, the N-atom is nearly planar as evidenced by the sum of angles about the N-atom (359.93° (**3a**) and 359.93° (**3b**)). Also, the average P–N bond distances in **3a** and **3b** are slightly shorter than those in the free diphosphinoamine ligands [24][36], which clearly indicate an enhancement of π-bonding in the P–N unit.

The Mo–P bond distances are 2.4925(10) and 2.5036(9) Å in **3a** and 2.4755(10) and 2.4898(9) Å in **3b**. The two Mo–P bond distances in **3a** or **3b** are relatively different. Apparently, the large steric constraints in the ligand prevent an appropriate orbital overlap when the two Mo–P bonds are equal and coplanar with the $Mo(CO)_4$ moiety. The average Mo–P bond distances in **3a** (2.498 Å) and **3b** (2.483 Å) are within the expected value range in comparison to similar *cis*-chelated tetracarbonylmolybdenum(0) complexes **5**–**9** (averaged 2.488 Å), slightly longer than those in tetracarbonyltungsten(0) complexes **13** and **14** (averaged 2.463 Å), and shorter than those in tetracarbonylchromium(0) complexes **10**–**12** (averaged 2.356 Å) due to the small atomic radius of chromium.

The Mo–C bond distances are 1.990(4)–2.039(5) Å for **3a** and 2.001(4)–2.048(5) Å for **3b**. The shorter Mo–C bond is *trans* to the longer Mo–P bond, which is in agreement with a *trans* effect of the donors (P < C≡O).

It is interesting to note that the Mo–P bond lengths in **15** and **16** (*Table 3*) are larger than those in **3a** and **3b**, which can be explained by the increased steric crowding caused by the two ligands in *cis* positions, while the Mo–P bond lengths in **17** are shorter than those in both **3a** and **3b**, probably due to relative *trans* influences of the phosphino and carbonyl ligands.

The P–Mo–P bite angles of **3a** and **3b** are much smaller than the P–Mo–P of the seven-membered ring in **18** (*Table 3*). We see that the P–M–P bite angle is dependent only on the ligand and the type of transition metal. The aromatic rings in **3a** and **3b**, as expected, have usual bond lengths and angles.

Conclusions. – We have shown the successful synthesis of group-6 transition metal tetracarbonyl complexes **2**–**4** of ligand **1**. All these new complexes were characterized by elemental analysis, IR, and multinuclear NMR spectroscopy. The ligand showed a clear tendency to coordinate in a *cis*-fashion to these transition metals, as indicated by ^{31}P-NMR spectroscopy. For the complex *cis*-[$Mo(CO)_4$(**1**)] (**3**), the molecular structure was determined.

We would like to thank the *Deanship of Scientific Research* at the Taibah University for funding (Res. No. 967/ 433).

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Received June 21, 2012