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A Convenient Solvothermal Synthesis of Group 6 PNP Pincer Tricarbonyl Complexes

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Supporting Information

ABSTRACT: The solvothermal synthesis of a series of zerovalent Cr, Mo, and W complexes of the type $[M(PNP)(CO)_3]$ featuring PNP pincer ligands based on 2,6-diaminopyridine is described. We demonstrate that the solvothermal synthesis technique presented provides a powerful, simple, and practical synthetic method resulting in high isolated yields in a short time. In particular, Cr and W complexes are not readily accessible via conventional methods. Moreover, this study allows a direct comparison of steric and electronic properties of group 6 metal PNP pincer tricarbonyl complexes.



INTRODUCTION

Among the many ligand systems that can be found in the chemical literature, pincer ligands play an important role and their complexes have attracted tremendous interest due to their high stability, activity, and variability.¹ These tridentate ligands are often planar scaffolds consisting of an anionic or neutral central aromatic backbone tethered to two, mostly bulky, phosphine donors by different spacers. In this family of ligands steric, electronic, and also stereochemical parameters can be manipulated by modifications of the substituents at the donor sites and/or the spacers. Accordingly, many applications of mostly precious transition-metal pincer complexes in the fields of catalysis, molecular recognition, and supramolecular chemistry were discovered, turning this area into an intensively investigated subject in organometallic chemistry.

Surprisingly, as far as group 6 pincer complexes are concerned, only a few examples have been reported in the literature.²⁻¹¹ For the first time, Haupt and co-workers prepared PNP pincer complexes of the type [M(PNP- $Ph)(CO)_{3}$ (M = Cr, Mo, W; PNP-Ph = N,N'-bis-(diphenylphosphino)-N,N'-2,6-diaminopyridine), albeit in low yields (19, 34, and 22%).² We are focusing on the chemistry of molybdenum and tungsten complexes containing PNP pincer ligands based on the 2,6-diaminopyridine scaffold, where the pyridine ring and the phosphine moieties are connected via NH, N-alkyl, or N-aryl linkers.⁴ These studies resulted in the preparation of halocarbonyl and hydridocarbonyl complexes of the types $[M(PNP)(CO)_3X]X$ (M = Mo, W; X = I, Br, Cl) (I), $[Mo(PNP)(CO)_2X_2]$ (X = I, Br, Cl, F) (II), [Mo(PNP)(CO)- X_2] (X = I, Br, Cl) (III), and [M(PNP)(CO)_3H]⁺ (M = Mo, W) (IV), as illustrated in Scheme 1.5^{-7} Analogous Cr complexes have, as yet, not been described. The synthesis of Scheme 1. Halo Carbonyl and Hydrido Carbonyl Mo(II) and W(II) PNP Pincer Complexes as a Function of the PR_2 Moieties and the NR' Spacers



a series of hydrido carbonyl and halo carbonyl tungsten pincer complexes featuring a related PNP pincer-type ligand based on silazane, viz. $HN(SiMe_2CH_2PPh_2)_2$, were described by Templeton and co-workers.⁸ Gambarotta et al. could show that the Cr(II) and Cr(III) PNP complexes [Cr(PNP-Ph)Cl₂] and $[Cr(PNP-Ph)Cl_2]$ (PNP-Ph = 2,6-bis-(diphenylphosphinomethyl)pyridine) are active catalysts for the oligomerization of ethylene.⁹ Recently, Schrock and coworkers showed¹⁰ that the molybdenum PCP pincer complex based on the 1,3-bis(phosphinito)benzene scaffold is capable of cleaving molecular dinitrogen to give a Mo(IV) PCP nitride complex. Another impressive reaction of group 6 PNP pincer complexes was discovered by the group of Nishibayashi.¹¹ They found that dinuclear molybdenum and tungsten dinitrogen complexes bearing bulky PNP pincer ligands (PNP = 2,6bis(dialkylphosphinomethyl)pyridines) are effective catalysts for the formation of ammonia from molecular dinitrogen. These few examples provide already a fortaste of the potential

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of group 6 pincer complexes with respect to stoichiometric and catalytic reactions involving, for instance, small molecules.

Accordingly, in order to further develop the chemistry of group 6 pincer systems, the availability of efficient synthetic protocols is essential. The most common synthetic entries into group 6 carbonyl complexes are the substitutionally inert hexacarbonyl complexes $M(CO)_{6}$, which are treated directly with a ligand under refluxing conditions in CH₃CN as a coordinating solvent stabilizing the labile $[M(CO)_3(CH_3CN)_3]$ intermediate. This reaction requires typically several hours for Cr and Mo but several days for W, with generally rather low vields in the case of Cr and W. Under conventional reaction conditions the use of $M(CO)_6$ complexes is also hampered by sublimation and deposition of the metal hexacarbonyl on the reflux condenser. The synthesis of transition-metal carbonyl complexes is sometimes significantly improved if the reactions are performed under microwave conditions.¹²⁻¹⁵ In some cases, special Teflon-lined vessels rather than simple glass vials were required.

In this paper, we report on the synthesis of the zerovalent Cr, Mo, and W complexes $[M(PNP)(CO)_3]$ featuring PNP pincer ligands based on the 2,6-diaminopyridine scaffold via a simple and fast solvothermal approach with no need for microwave equipment.¹⁶ All reactions are performed in standard aluminum-capped, microwave glass vials which allow the generation of higher pressures and superheating of the solvent. This results in significantly decreased reaction times and highly increased product yields in a clean fashion over methodologies reported using traditional procedures. Moreover, this study allows comparisons among a complete series of Cr, Mo, and W PNP tricarbonyl complexes as far as electronic and steric properties are concerned.

RESULTS AND DISCUSSION

A suspension of hexacarbonyl complexes $M(CO)_6$ and PNP ligands 1a-j in CH₃CN were placed in a sealed microwave glass tube and stirred for 2–5 h at 135–160 °C. After workup, the analytically pure products 2–4 were obtained in 78–99% isolated yields (Scheme 2). Several years ago Haupt and coworkers reported the synthesis of $[M(PNP-Ph)(CO_3)]$ (M = Cr, Mo, W) (2e–4e).²

We reported recently a comparatively time consuming threestep synthesis of W(0) complexes $[W(PNP)(CO)_3]$ via the dinuclear complex $[W(CO)_4(\mu$ -Br)Br]_2, prepared in situ from $W(CO)_6$ and stoichiometric amounts of Br₂. Treatment of $[W(CO)_4(\mu$ -Br)Br]_2 with the PNP ligands **1b**,d,e afforded the tungsten(II) intermediates $[W(PNP)(CO)_3Br]Br$, which subsequently were reduced with sodium amalgam to yield the W(0) complexes **4b**, **1d**, and **4e** in 56, 46, and 68% overall yields, respectively (Scheme 3).⁹

All complexes were fully characterized by a combination of ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectroscopy, IR spectroscopy, and elemental analysis. Characteristic features comprise, in the ¹³C{¹H} NMR spectrum, two low-field triplet resonances (1:2 ratio) in the range of 240–196 ppm assignable to the carbonyl carbon atoms *trans* and *cis* to the pyridine nitrogen, respectively. The ³¹P{¹H} NMR spectra exhibit singlet resonances with ¹J_{WP} coupling constants of 315–494 Hz in the case of tungsten complexes (Table 1).

The tungsten-phosphorus coupling was observed as a doublet satellite due to ¹⁸³W (14% abundance with I = 1/2) superimposed over the dominant singlet. Both the carbonyl resonances (δ_{co}) and the phosphorus resonances (δ_{p}) exhibit a

Scheme 2. Synthesis of $[M(PNP)(CO)_3]$ (M = Cr, Mo, W) Complexes under Solvothermal Conditions in CH₃CN^{*a*}



^{*a*}Labeling of complexes refers to letters of ligands depicted here.

Scheme 3. Three-Step Synthesis of W(0) Complexes via $[W(CO)_4(\mu$ -Br)Br]_2 and $[W(PNP)(CO)_3Br]Br$ Intermediates



significant upfield shift on going from Cr to Mo to W (Table 1). The IR spectra show, in most cases, the typical three strong to medium absorption bands of a *mer* CO arrangement in the range of 1985–1756 cm⁻¹ assignable to one weaker symmetric and two strong asymmetric ν_{CO} stretching modes. The ν_{CO} frequencies, in particular the symmetric CO stretch, is indicative of increasing electron donor strengths of the PNP ligands and follow roughly the order PNP-BIPOL < PNP-Ph < PNP^{Me}-Ph < PNP-Cy < PNP-*i*Pr \approx PNP^{Me}-*i*Pr < PNP-Et < PNP-*t*Bu (Table 2).

In addition to spectroscopic characterization, the solid-state structures of **2a,b,d** were determined by single-crystal X-ray diffraction. Structural views are depicted in Figures 1 and 2 with selected bond distances given in the captions (the structure of **2b** is provided in the Supporting Information).

The coordination geometry around the chromium center, as in the case of analogous Mo and W complexes,^{2,6,7} corresponds to a distorted octahedron. In particular, the carbonyl–metal–

Table 1. Selected	${}^{13}C{}^{1}H$ and ${}^{31}P{}^{1}$	¹ H} NMR Data of
$[M(PNP)(CO)_3]$	(M = Cr, Mo, W)	Complexes

	metal						
	Cr		Мо		W		
ligand	$\delta_{\rm CO}$, ppm	$\delta_{ ext{P}}$, ppm	$\delta_{\rm CO}$, ppm	$\delta_{ ext{P}}$, ppm	$\delta_{\rm CO}$, ppm	$\delta_{ ext{P}}$, ppm	
1a	235.7	130.0	230.3	111.3	222.0	94.0	
	223.8		213.8		208.2		
1b	236.2	146.7	231.4	143.6	221.1	128.5	
	225.6		216.9		210.6		
1c	236.1	149.7	231.1	122.6	222.3	106.5	
	225.8		216.4		211.3		
1d	238.7	164.4	233.1	161.9	224.7	147.2	
	233.0		224.0		219.4		
1e	234.6	125.7	228.4	116.2	206.0	100.2	
	220.6		211.2		196.6		
1f	235.2	171.5	230.8	159.0	222.5	144.0	
	226.0		217.9		211.6		
1g	223.4	152.1	227.8	131.0	221.1	114.7	
	220.8		211.9		207.4		
1h	234.8	147.8	229.9	129.5	221.7	112.7	
	222.8		214.3		208.4		
1i	230.2	230.0	224.7	204.8	215.5	188.2	
	217.9		208.4		201.4		
1j	236.2	193.5					
	223.9						

carbonyl angles of the CO ligands *trans* to one another deviate significantly from 180°. They vary with the bulkiness of the PR₂ moiety and decrease from 166.68(4)° in $[Cr(PNP-Et)(CO)_3]$ (2a) to 164.04(1)° in $[Cr(PNP-iPr)(CO)_3]$ (2b) to 155.22(5)° in $[Cr(PNP-tBu)(CO)_3]$ (2d). The same trend is found in the analogous Mo and W complexes: 171.1(8)° in $[Mo(PNP-Ph)(CO)_3]$ (3d), 166.03(5)° in $[Mo(PNP-iPr)(CO)_3]$ (3b), 162.93(7)° in $[Mo(PNP^{Me}-iPr)(CO)_3]$ (3f), 156.53(4)° in $[Mo(PNP-tBu)(CO)_3]$ (3d), 165.7(2)° in $[W(PNP-iPr)(CO)_3]$ (4b), and 156.46(9)° in $[W(PNP-tBu)(CO)_3]$ (4d). Accordingly, the bulkiness of the PNP ligands follows roughly the order (PNP-Ph \approx PNP-Et < PNP-*i*Pr₂ < PNP^{Me}-*i*Pr < PNP-*t*Bu).

In summary, we demonstrated that the solvothermal synthesis technique provides a powerful, simple, and practical synthetic method to afford group 6 PNP pincer carbonyl complexes of the type $[M(PNP)(CO)_3]$ (M = Cr, Mo, W) in high isolated yields in a short time. It has to be emphasized that in particular the short reaction times allow the use of thermally more sensitive ligands. As far as Cr and W complexes are concerned, these complexes are not readily accessible with





Figure 1. Structural view of $[Cr(PNP-Et)(CO)_3]$ (2a) showing 50% thermal ellipsoids (H atoms omitted for clarity). Selected bond lengths (Å) and bond angles (deg): Cr1–P1 2.2678(3), Cr1–P2 2.2724(3), Cr1–C14 1.8704(9), Cr1–C15 1.8295(10), Cr1–C16 1.18551(9), Cr1–N1 2.139(1); P1–Cr1–P2 160.03(1), C14–Cr1–C16 166.68(4).



Figure 2. Structural view of $[Cr(PNP-tBu)(CO)_3]$ ·CH₃CN (2d·CH₃CN) showing 50% thermal ellipsoids (H atoms and CH₃CN) omitted for clarity). Selected bond lengths (Å) and bond angles (deg): Cr1–P1 2.3627(4), Cr1–P2 2.3706(4), Cr1–22 1.864(1), Cr1–C23 1.793(1), Cr1–C24 1.867(1), Cr1–N1 2.187(1); P1–Cr1–P2 154.76(1), C22–Cr1–C24 155.22(5).

conventional methods. Moreover, this study also allows a direct comparison of steric and electronic properties of group 6 metal PNP pincer complexes.

EXPERIMENTAL SECTION

General Considerations. All manipulations were performed under an inert atmosphere of argon by using Schlenk techniques or in an MBraun inert-gas glovebox. The solvents were purified according to standard procedures.¹⁷ The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. The ligands PNP-Et (1a),¹⁸ PNP-*i*Pr (1b),⁴ PNP-Cy (1c),¹⁹ PNP-*t*Bu (1d),⁴ PNP-Ph (1e),² PNP^{Me}-*i*Pr (1f),⁷ PNP^{Me}-Ph (1g),⁵ PNP^{Ph}-Et (1h),¹⁹ and PNP-BIPOL⁴ (1i) were prepared according to the literature. The synthesis of PNP-SPEA (1j) is described in the Supporting Information. ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectra were recorded on Bruker AVANCE-250 and AVANCE-400 spectrometers. ¹H and ¹³C{¹H} NMR spectra were referenced internally to residual protio solvent and solvent resonances, respectively, and are reported relative to tetramethylsilane (δ 0 ppm). ³¹P{¹H} NMR spectra were referenced

Table 2. Carbonyl Stretching Frequencies (ν_{CO} , cm⁻¹) of [M(PNP)(CO)₃] (M = Cr, Mo, W) Complexes

	ligand									
metal	1a	1b	1c	1d	1e	1f	1g	1h	li	1j
Cr	1905	1923	1913	1908	1973	1926	1954	1945	1972	1936
	1821	1785	1807	1792	1840	1795	1842	1807	1860	1827
	1763		1793	1756	1807	1774	1819			1811
Mo	1929	1936	1941	1922	1964	1936	1956	1949	1985	
	1840	1809	1828	1808	1858	1810	1911	1815	1876	
	1780	1790	1790	1771	1765	1795	1850			
W	1921	1929	1933	1914	1955	1928	1954	1934	1979	
	1834	1805	1807	1799	1847	1890	1839	1804	1858	
	1768	1784	1790	1759	1759	1797	1801			

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externally to H_3PO_4 (85%) (δ 0 ppm). Aluminum-capped 20 mL microwave vials from Biotage or VWR were used as reaction vessels.

General Procedure for the Synthesis of $[M(PNP)(CO)_3]$ (M = Cr, Mo, W). A suspension of the metal hexacarbonyl (0.60 mmol) and 1.1 equiv of the respective PNP ligand (0.63 mmol) in acetonitrile (3 mL) were placed in a 20 mL sealed glass tube and stirred for 2 h at 135 °C (unless otherwise noted; see the Supporting Information), whereupon a clear solution was obtained. The reaction mixture was cooled to room temperature without stirring. In most cases the product was obtained as a crystalline material and was decanted and washed with *n*-hexane. In all other cases the solvent was removed under reduced pressure. The remaining solid was washed with *n*-hexane and dried under vacuum. Complexes 2a-j, 3a-i, and 4a-i were obtained in 77–99% isolated yields.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00940.

Experimental procedures, characterization data of all complexes, and crystallographic details of **2a**, **2b**· CH₃CN, and **2d**·CH₃CN (PDF)

Crystallographic data for 2a, $2b \cdot CH_3CN$, and $2d \cdot CH_3CN$ (CIF)

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Notes

The authors declare no competing financial interest.

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