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Synthesis, crystal and molecular structure of a binuclear, double-bridged hexacarbonyl tungsten derivative of 4-pyridyldiphenylphosphane

Leeni Hirsivaara [a,]*, Matti Haukka [b], Jouni Pursiainen [a]

[a] *Department of Chemistry, University of Oulu, PO Box 3000, FIN-90014 Oulu, Finland*
[b] *Department of Chemistry, University of Joensuu, PO Box 111, FIN-80101 Joensuu, Finland*

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Abstract

4-Pyridyldiphenylphosphane is used as a bridging ligand for the first time. The ligand forms a double-bridged bimetallic complex with hexacarbonyl tungsten. Characterization is performed by X-ray analysis and NMR spectroscopy. The crystal structure of the complex shows π-stacking interaction between the pyridyl rings, and structurally the complex is an organometallic analogue of [2.2]-paracyclophanes. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Bimetallic transition metal complexes usually have the metal centers close to each other, often with direct metal-to-metal interactions. Bridging ligands, like chloride or 2-pyridyldiphenylphosphane [1], are typically used to enhance the stability of the structures. To combine two distant metal atoms together, ligands like semiquinones [2], bipyridines [3] or some ladder-like ligands [4] are used. Such ligands can, for example, also be used in self-organizing structures in supramolecular chemistry [5].

In this paper, we report the use of 4-pyridyldiphenylphosphane as a novel type of bridging phosphane ligand between two metal centers in a double-bridged structure of $[W(CO)_4(P(4\text{-py})Ph_2)]_2$, with π-stacked pyridine rings. Complex $[W(CO)_4(P(4\text{-py})Ph_2)]_2$, in which both tungsten atoms occupy one W–N and one W–P bond, is prepared and characterized with X-ray analysis and NMR spectrometry. This complex is the first 4-pyridylphosphane-bridged binuclear transition metal complex reported. The only phosphane ligands that are used as the 4-pyridylphosphane-type bridge are the diphenylphosphino-terpyridines in trimetallic systems [6]. However, Cu(I) and Cd(II) derivatives of ligand 4-thiomethyl-6-(3-pyridyl)-2,2′-bipyridine, which are structurally closely related to $[W(CO)_4(P(4\text{-py})Ph_2)]_2$, have been reported [7].

2. Experimental

2.1. Synthesis of $[W(CO)_4(P(4\text{-py})Ph_2)]_2$

$[W(CO)_4(py)_2]$ (504 mg, 1.11 mmol) was partly dissolved in benzene (40 ml). 4-Pyridyldiphenylphosphane (585 mg, 2.22 mmol) was added and the mixture was stirred for 24 h at 40–45 °C temperature. The reaction was carried out in nitrogen atmosphere. Purification was performed by column chromatography using first a dichloromethane:hexane (2:1) mixture, and then dichloromethane as eluent. Yield 160 mg (17%). Crystals were grown by slow evaporation of dichloromethane–hexane mixture. ^{1}H-NMR δ_H (see Fig. 1 for numbering): $H_{6,10,12,16}$: 7.76 (m); $H_{7-9,13-15}$: 7.48 (m); $H_{18,22}$: 6.65 (dd); $H_{19,21}$ 8.23 (d). ^{13}C-{^{1}H}-NMR δ_C (Fig. 1 for numbering): C_1: 203.65 (d, $^2J_{CP} =$

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* Corresponding author. Tel.: + 358-8-5531647; fax: + 358-8-5531603.

E-mail address: leeni.hirsivaara@oulu.fi (L. Hirsivaara).

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7.3 Hz); $C_{2,3}$: 198.85 (s); C_4: 208.5 (d); $C_{5,11}$: 132.38 (d, $^1J_{C-P} = 41.9$ Hz); $C_{6,10,12,16}$: 133.93 (d, $^2J_{C-P} = 12.9$ Hz); $C_{7,9,13,15}$: 129.16 (d, $^3J_{C-P} = 10.2$ Hz); $C_{8,14}$: 131.25 (s); C_{17}: 145.93 (d, $^1J_{C-P} = 22.3$ Hz); $C_{18,22}$: 128.89 (d, $^2J_{C-P} = 9.2$ Hz); $C_{19,21}$: 154.40 (d, 6.7 Hz). ^{31}P-{^1H}-NMR: δ_P 35.1 ppm ($^1J_{W-P} = 240$ Hz). IR (CH_2Cl_2) cm^{-1} 2012 (s), 1893 (vs, wide), 1857 (s) (C=O). Elemental analysis could not be obtained because of gradual decomposition of the complex when dried.

2.2. Synthesis of P(4-py)Ph$_2$ ligand

The ligand P(4-py)Ph$_2$ is known previously from literature [8,9]. In this work, the ligand was prepared by the method used previously for the preparation of 2-pyridylphosphanes [10]. The starting material, 4-bromopyridine, was obtained by dissolving 4-bromopyridine hydrochloride (Aldrich) in distilled, deoxygenated water. NaOH (10%) was added until the solution became basic. The resulting 4-bromopyridine was extracted with diethyl ether and dried in vacuum. Synthesis was continued as described elsewhere [10]. The resulting ligand was not pure enough after purification by extraction, and was further purified by column chromatography using first dichloromethane, and then 3:1 dichloromethane:acetonitrile as eluent. ^1H-NMR δ_H (see Fig. 1 for numbering): $H_{6-10,12-16}$: 7.32–7.41; $H_{18,22}$: 7.11 (m); $H_{19,21}$ 8.51 (m). ^{13}C-{^1H}-NMR δ_C (Fig. 1 for numbering): $C_{5,11}$: 134.90 (d, $^1J_{C-P} = 10$ Hz); $C_{6,10,12,16}$: 134.16 (d, $^2J_{C-P} = 20$ Hz); $C_{7,9,13,15}$: 128.80 (d, $^3J_{C-P} = 8$ Hz); $C_{8,14}$: 129.51 (s); C_{17}: 134.90 (d, $^1J_{C-P} =$ 10 Hz); $C_{18,22}$: 127.20 (d, $^2J_{C-P} = 15$ Hz); $C_{19,21}$: 149.25 (d, 4 Hz). ^{31}P–{^1H}-NMR: δ_P – 5.3 ppm.

2.3. Spectroscopy

^1H-NMR spectra (400 MHz, Me_4Si), ^{13}C-{^1H}-NMR spectra (100 MHz, Me_4Si), two-dimensional heteronuclear single quantum correlation (HSQC) spectra and ^{31}P-{^1H}-NMR spectra (162 MHz, ext. stand. 85% H_3PO_4) were recorded on a Bruker DPX 400 spectrometer in $CDCl_3$ (CIL, D 99.8%, 0.03% Me_4Si). IR spectra were measured on a Bruker IFS 66 spectrometer in dichloromethane (99.8%).

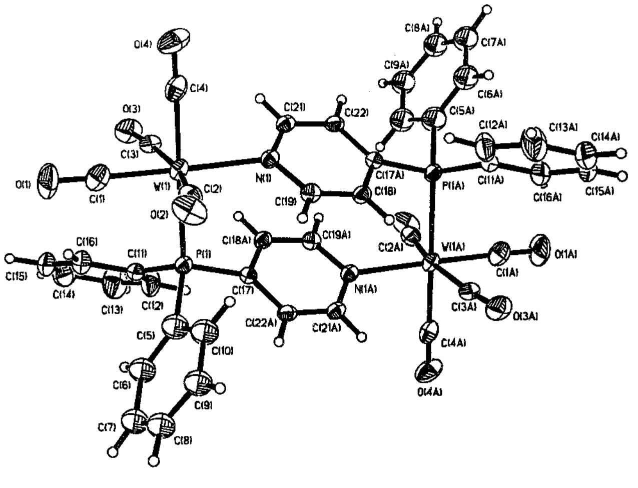

Fig. 1. X-ray structure of complex [W(CO)$_4$(P(4-py)Ph$_2$)]$_2$.

2.4. Crystal structure determination

$C_{21}H_{14}NO_4PW$, $M = 559.15$, triclinic, $a = 8.6451(2)$ Å, $b = 9.1862(2)$ Å, $c = 12.7328(3)$ Å, $\alpha = 80.4810(10)°$, $\beta = 89.2110(10)°$, $\gamma = 82.9380(10)°$, $V = 989.67(4)$ Å^3, $T = 150$ K, space group $P\bar{1}$ (no. 2), $Z = 2$, $D_c = 1.876$ g cm^{-3}, $\mu(MoK_\alpha) = 5.943$ mm^{-1}, 11 555 reflection collected, 3578 unique ($R_{int} = 0.0175$). The final R_1 was 0.0201 (all data) and $wR_2(F^2) = 0.0468$ (all data). Data were collected with a Nonius KappaCCD diffractometer using MoK_α radiation ($\lambda = 0.710 73$ Å). Hydrogen atoms were placed on calculated positions and constrained to ride with the parent atom. One of the phenyl rings in the asymmetric unit was disordered in two positions, having population parameters of 0.70 and 0.30. In the latter position the carbon–carbon bond lengths were fixed to 1.39 Å and the anisotropic displacement parameters were constrained to be equal for all carbon atoms. The carbon atoms in the ring of higher population were refined anisotropically with equal anisotropic displacement parameters. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC 158094 for compound [W(CO)$_4$(P(4-py)Ph$_2$)]$_2$.

3. Results and discussion

Complex [W(CO)$_4$(P(4-py)Ph$_2$)]$_2$ was synthesized by an overnight reaction between [W(CO)$_4$(py)$_2$] and 4-pyridyldiphenylphosphane ligand in benzene solution at 40–45 °C [11], and purified by column chromatography. The product was not particularly air sensitive, but slowly decomposed in the course of time. Single crystals of the complex disassembled easily if they were allowed to dry in air.

The X-ray structure of the complex [W(CO)$_4$(P(4-py)Ph$_2$)]$_2$ is presented in Fig. 1, and the bond lengths and angles around the metal centers are presented in Table 1. The octahedral environment around the metal centers is slightly distorted: the N–W–P angle is 88.46(7)°, and the carbonyl groups are pushed away from the phosphane ligand. The carbonyl group trans to phosphorus has slightly shortened C–W and C–O bonds compared with cis carbonyl groups, and the carbonyl group trans to the nitrogen atom has them clearly shortened, reflecting the differences in the relative trans effects of the N, P and CO donors.

Table 1
Bond lengths (Å) and angles (°) around the metal center for complex $[W(CO)_4(P(4\text{-py})Ph_2)]_2$

Bond lengths			
W–P(1)	2.5488(9)	C(1)–O(1)	1.167(5)
W–N(1)	2.268(3)	C(2)–O(2)	1.138(4)
W–C(1)	1.950(4)	C(3)–O(3)	1.145(4)
W–C(2)	2.040(4)	C(4)–O(4)	1.143(4)
W–C(3)	2.019(3)		
W–C(4)	2.005(4)		
Bond angles			
P(1)–W–C(1)	92.04(12)	P(1)–W–N(1)	88.46(7)
P(1)–W–C(2)	96.43(10)	N(1)–W–C(1)	178.74(12)
P(1)–W–C(3)	86.76(9)	N(1)–W–C(2)	96.76(12)
P(1)–W–C(4)	174.71(11)	N(1)–W–C(3)	96.44(12)
P(1)–W–N(1)	88.46(7)	N(1)–W–C(4)	89.43(13)
N(1)–W–C(1)	178.74(12)	C(1)–W–C(2)	84.34(15)
N(1)–W–C(3)	96.44(12)	C(1)–W–C(3)	82.44(15)
N(1)–W–C(4)	89.43(13)	C(1)–W–C(4)	89.97(16)
P(1)–W–C(1)	92.04(12)	C(2)–W–C(3)	166.50(15)
P(1)–W–C(2)	96.43(10)	C(2)–W–C(4)	88.64(14)
P(1)–W–C(3)	86.76(9)	C(3)–W–C(4)	88.65(13)
P(1)–W–C(4)	174.71(11)		

Pyridyl rings between the tungsten units are parallel with angle of 0(1)°, and the distance between the centers of the rings is 3.286 Å, indicating face-to-face π-stacking interaction. The distance between the rings is quite short compared with the normal attractive π-stacking distance between the pyridyl centroids (which is between 3.3 and 3.8 Å [12]) or with the mononuclear complex *cis*-$[W(CO)_4(P(2\text{-py})Ph_2)_2]$ [13] (which possesses a related face-to-face π-stacking interaction with a distance of 3.902 Å between the centers of the pyridyl rings, and an angle of 7.18(7)° between the pyridyl rings). The difference between the π-stacking distances in the complexes may be due to steric reasons in a binuclear complex, or due to relative differences in the ring polarization influences of the N atoms of the two structures [14]: in the binuclear structure, the N atoms are in the opposite edges of the aryl rings, whereas in the case of mononuclear *cis*-$[W(CO)_4(P(2\text{-py})Ph_2)_2]$ the N atoms are in adjacent positions.

^1H-, ^{13}C-$\{^1H\}$- and ^{31}P-$\{^1H\}$-NMR data for both the complex and the free ligand are presented in the Section 2. The interpretation of the ^1H- and ^{13}C-$\{^1H\}$-NMR spectra was performed with the help of two-dimensional HSQC spectra. Chemical shifts of the pyridyl protons are lowered due to coordination of the ligand, whereas the chemical shifts of the phenyl protons are increased. In the ^{13}C-NMR spectroscopy, the chemical shifts of the pyridyl carbon atoms are increased, whereas the chemical shifts of the phenyl carbon atoms are not remarkably affected by coordination.

Interestingly, the complex $[W(CO)_4(P(4\text{-py})Ph_2)]_2$ is structurally an organometallic analogue of [2.2]-paracyclophanes, particularly of pyridinophanes [15]. On the other hand, the ability of the ligand $P(4\text{-py})Ph_2$ to form bridges makes it a possible building unit for organometallic polymers.

Acknowledgements

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