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**Crystal structure of hexacarbonyl-( $\mu_2$ -methanoato- $\kappa_2O:O'$ )-( $\mu_2$ -bis(di-p-tolylphosphino)cyclohexylamine- $\kappa_2P:P'$ )dirhenium(I),  
C<sub>42</sub>H<sub>45</sub>N<sub>0</sub>S<sub>2</sub>Re<sub>2</sub>**

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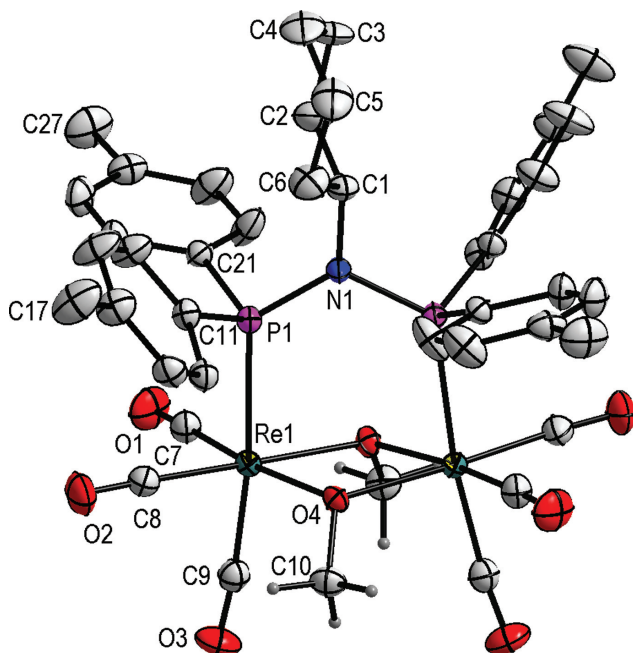
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## Crystal structure of hexacarbonyl-( $\mu_2$ -methanoato- $k^2O:O'$ )-( $\mu_2$ -bis(di-*p*-tolylphosphino)cyclohexylamine- $\kappa^2P:P'$ )dirhenium(I), $C_{42}H_{45}NO_8P_2Re_2$



The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

**Table 1:** Data collection and handling.

Crystal:	Colourless cube
Size:	0.30 × 0.22 × 0.10 mm
Wavelength:	Mo K $\alpha$ radiation (0.71073 Å)
$\mu$ :	6.17 mm $^{-1}$
Diffractometer, scan mode:	Xcalibur, $\omega$
$\theta_{max}$ , completeness:	28.0°, >99%
$N(hkl)_{measured}$ , $N(hkl)_{unique}$ , $R_{int}$ :	20362, 4842, 0.049
Criterion for $I_{obs}$ , $N(hkl)_{gt}$ :	$I_{obs} > 2 \sigma(I_{obs})$ , 4325
$N(param)_{refined}$ :	280
Programs:	CrysAlis <sup>PRO</sup> [1], SHELX [2, 3], Diamond [4], Olex2 [5]

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### Abstract

$C_{42}H_{45}NO_8P_2Re_2$ , monoclinic,  $C2/c$  (no. 15),  $a = 24.1612(7)$  Å,  $b = 13.0229(3)$  Å,  $c = 14.9180(4)$  Å,  $\beta = 121.383(3)^\circ$ ,  $V = 4007.2(2)$  Å $^3$ ,  $Z = 4$ ,  $R_{gt}(F) = 0.0235$ ,  $wR_{ref}(F^2) = 0.0596$ ,  $T = 173(2)$  K.

CCDC no.: 1959602

### Source of material

*N,N*-Bis(di-*p*-tolylphosphino)cyclohexylamine: Cyclohexylamine (230  $\mu$ L, 2.011 mmol) and triethylamine (2.2 mL, 15.8 mmol) were dissolved in a dried DCM (15 mL) and the reaction mixture was then stirred under an ice bath. Chloro-di(*p*-tolyl)phosphine (2.0 mL, 8.85 mmol) was then added to the reaction. The ice bath was removed after 30 min and the reaction was stirred at room temperature for an additional 12 h. The product was extracted with DCM and a white solid product (0.565 g, 54%) was obtained after solvent evaporation.  $^1H$  NMR (400.13 MHz,  $CD_2Cl_2$ , 25 °C):  $\delta_H$  [ppm] 2.23 (3H, s, 1 CH $_3$ ), 6.51 (2 H, d,  $J = 8.0$  Hz, 2 CH), 6.77 (2 H, d,  $J = 8.1$  Hz, 2 CH), 7.30 (20 H, m, 20 CH).  $^{31}P$  NMR (161.97 MHz,  $CD_2Cl_2$ , 25 °C,  $H_3PO_4$ ):  $\delta_P$  68.60 (s).

**Title complex:** The product was obtained as a by-product of the reaction,  $(NEt_4)_2[Re(CO)_3(Br)_3]$  (53.1 mg, 0.0688 mmol) dissolved in 10 mL methanol, mixed with *N,N*-bis(di-*p*-tolylphosphino) cyclohexylamine (34.1 mg, 0.0649 mmol) dissolved in DCM (5 mL). The reaction was stirred at 50 °C for 2 h whereafter the solvent was evaporated. The resulting white solid was filtered and washed with methanol then dissolved in dichloromethane and layered with methanol and left to recrystallize. The amount of crystals obtained was too small for us to perform other characterization techniques besides single-crystal X-ray diffraction analyses.

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**Table 2:** Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>).

Atom	x	y	z	$U_{iso}^*/U_{eq}$
Re1	0.58118(2)	0.47544(2)	0.30458(2)	0.01828(5)
P1	0.57253(4)	0.28372(6)	0.30657(6)	0.01877(16)
O1	0.66629(15)	0.4689(2)	0.2088(3)	0.0434(7)
O2	0.70610(13)	0.4610(2)	0.5205(2)	0.0424(7)
O3	0.61366(14)	0.70554(19)	0.3340(2)	0.0410(7)
O4	0.50841(11)	0.48377(15)	0.34506(17)	0.0197(5)
N1	0.50000	0.2205(3)	0.25000	0.0287(9)
C1 <sup>a</sup>	0.5086(4)	0.1046(5)	0.2371(7)	0.0241(17)
H1 <sup>a</sup>	0.556581	0.094189	0.279693	0.029*
C2 <sup>b</sup>	0.4838(5)	0.0431(6)	0.2942(8)	0.038(2)
H2A <sup>b</sup>	0.435990	0.048198	0.256494	0.046*
H2B <sup>b</sup>	0.501635	0.071465	0.365639	0.046*
C3 <sup>b</sup>	0.5035(6)	-0.0687(7)	0.3017(9)	0.044(3)
H3A <sup>b</sup>	0.550857	-0.074524	0.351472	0.052*
H3B <sup>b</sup>	0.481587	-0.109112	0.330528	0.052*
C4 <sup>a</sup>	0.4871(6)	-0.1144(7)	0.1976(9)	0.053(3)
H4A <sup>a</sup>	0.505993	-0.184083	0.209492	0.063*
H4B <sup>a</sup>	0.439407	-0.121072	0.152260	0.063*
C5 <sup>c</sup>	0.5115(5)	-0.0512(6)	0.1421(8)	0.047(3)
H5A <sup>c</sup>	0.495894	-0.080693	0.071679	0.057*
H5B <sup>c</sup>	0.559528	-0.053007	0.181971	0.057*
C6 <sup>c</sup>	0.4889(4)	0.0589(6)	0.1306(7)	0.036(2)
H6A <sup>c</sup>	0.441146	0.061558	0.084157	0.043*
H6B <sup>c</sup>	0.508098	0.100007	0.097694	0.043*
C7	0.63491(18)	0.4684(2)	0.2450(3)	0.0269(7)
C8	0.65878(18)	0.4640(2)	0.4412(3)	0.0295(8)
C9	0.59822(17)	0.6212(3)	0.3189(3)	0.0266(7)
C10	0.51434(17)	0.5646(3)	0.4137(3)	0.0286(7)
H10A	0.555539	0.557644	0.480574	0.043*
H10B	0.478362	0.560876	0.426108	0.043*
H10C	0.513205	0.630810	0.381605	0.043*
C11	0.61475(15)	0.2327(2)	0.4400(2)	0.0218(6)
C12	0.59915(15)	0.2794(3)	0.5081(2)	0.0249(7)
H12	0.573836	0.340372	0.486723	0.030*
C13	0.61998(17)	0.2384(3)	0.6068(3)	0.0284(7)
H13	0.607712	0.270622	0.651011	0.034*
C14	0.65837(19)	0.1513(3)	0.6413(3)	0.0337(8)
C15	0.6754(2)	0.1069(3)	0.5748(3)	0.0426(10)
H15	0.702661	0.048100	0.597864	0.051*
C16	0.65379(19)	0.1458(3)	0.4752(3)	0.0339(8)
H16	0.665750	0.112920	0.430889	0.041*
C17	0.6830(2)	0.1061(3)	0.7492(3)	0.0486(11)
H17A	0.730077	0.115346	0.792625	0.073*
H17B	0.672644	0.032746	0.742582	0.073*
H17C	0.662210	0.141122	0.782249	0.073*
C21	0.61410(15)	0.2363(2)	0.2422(2)	0.0213(6)
C22	0.58046(19)	0.2376(3)	0.1329(3)	0.0371(9)
H22	0.535541	0.253762	0.094648	0.044*
C23	0.6115(2)	0.2159(3)	0.0793(3)	0.0397(9)
H23	0.587404	0.217767	0.004730	0.048*
C24	0.67668(18)	0.1913(3)	0.1314(3)	0.0301(8)
C25	0.70951(17)	0.1906(3)	0.2400(3)	0.0340(8)
H25	0.754196	0.172912	0.278104	0.041*
C26	0.67974(16)	0.2145(3)	0.2948(3)	0.0275(7)
H26	0.704463	0.216029	0.369383	0.033*
C27	0.7106(2)	0.1713(3)	0.0718(3)	0.0454(10)
H27A	0.721327	0.236923	0.052334	0.068*
H27B	0.681879	0.131837	0.008227	0.068*
H27C	0.750423	0.132338	0.116296	0.068*

<sup>a</sup>Occupancy: 0.5, <sup>b</sup>Occupancy: 0.496(10), <sup>c</sup>Occupancy: 0.504(10).

## Experimental details

H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C–H = 0.95 and 0.98 Å and  $U_{iso}(H) = 1.2U_{eq}(C)$  and  $1.5U_{eq}(C)$  respectively. The highest peak (1.48 e. Å<sup>-3</sup>) is located 0.42 Å away from C29 and the deepest hole (-1.28 e. Å<sup>-3</sup>) is located 0.3 Å away from C29.

## Comment

Dirhenium(I) hexacarbonyl complexes exhibit properties such as high carbonyl ligand kinetic stability due to their 'low lying metal to ligand charge transfer' (MLCT) state. For this reason, dirhenium(I) hexacarbonyl complexes consisting of bridging bis(chelating) ligands have enjoyed significant attention in various fields such as photoluminescence, anti-cancer pharmaceuticals and catalysis [5–10]. However, these attributes are already well known in the chemistry of halogenated/aqueous tricarbonyl (*fac*-[M(CO)<sub>3</sub>]<sup>+</sup>) complexes of the group 7 transition elements (M = Mn, Tc and Re) [11, 12]. By way of comparison, it is however evident that there is still much outstanding research on dirhenium complexes [6–19]. Nonetheless, it has been suggested in literature that two heavy metals bridged with a chelating ligand enhances the emissive properties of the metal orbitals involved, suggesting that di-nuclear species might offer a greater advantage over their mono-nuclear counter parts. This is particularly more advantageous for fields such as photoluminescence [6]. The versatility of diphosphinoamine (PNP) bis(chelating) ligands have on the other hand fueled the interest in developing highly selective homogeneous catalysts. The strong electron donating ability of the diphosphinoamine (PNP) ligands makes it easy for these chelating ligands to be coordinated to various transition metals [19]. Thus, in the above-mentioned complex we have the advantage of having two bridged heavy metals, but we also have a chelating ligand that can easily be tuned both sterically and electronically. This complex was obtained serendipitously as a byproduct during the synthesis and crystallization of *fac*-[Re{bis(di-*p*-tolylphosphino)cyclohexylamine}(CO)<sub>3</sub>Br].

The title complex crystallizes in the monoclinic crystal system in the *C2/c* space group, with four formula units ( $Z = 4$ ) in the unit cell. The asymmetric unit contains half of the title complex while the other half is generated through the (1 - x, +y, 1/2 - z) symmetry. A comparison of the core geometry (Re–O–Re–O; across the two Re(I) centres and the two bridging methanolato ligands) indicates that the title complex adopts an almost planar geometry with a bent angle of only 7.35° around the O–O axis which is significantly smaller when compared to the two similar structures found in the Cambridge Structural Database (Version 5.39, November 2017). These exhibit bent angles of 27.10° and 35.69° (CCDC

Ref. codes ZIYSAB and CIHXOG), respectively [20, 21]. This difference is likely due to the steric demand exerted by the methanolate groups on the geometrical core of the complex. All the other bond lengths and bond angles are comparable to that reported in literature.

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