

Conformation analysis of triphenylphosphine in *trans* and *cis* triphenylphosphine-substituted Fischer carbene complexes



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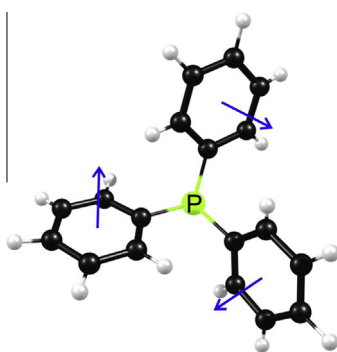
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HIGHLIGHTS

- Synthesis of novel [(CO)₄(PPh₃)M(OEt)(aryl)-carbene] complexes, M = Cr or Mo.
- First crystal structure of a *trans*-[(CO)₄(PPh₃)M-carbene], M = W.
- Crystal structures of *cis*-[(CO)₄(PPh₃)M-carbene] complexes.
- PPh₃ orientation in octahedral *trans*- and *cis*-[(CO)₄(PPh₃)M-carbene] complexes.
- Remarkable performance of DFT to determine PPh₃ orientation.

GRAPHICAL ABSTRACT

Orientation of triphenylphosphine in octahedral [(CO)₄(PPh₃)W-carbene] complexes.



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ABSTRACT

The synthesis and selected crystal structures of novel (M = Cr or Mo) and known (M = W) [(CO)₄(PPh₃)M = C(OEt)R] complexes, M = Cr, R = 2-thienyl (**1**), 2-furyl (**2**); M = Mo, R = 2-thienyl (**3**), 2-furyl (**4**); M = W, R = 2-thienyl (**5**), 2-furyl (**6**), are presented. Experimental crystal structures and DFT calculations of selected *trans*- and *cis*-triphenylphosphine-substituted Fischer carbene complexes, illustrate that the minimum energy conformation of triphenylphosphine (PPh₃) in octahedral [(CO)₄(PPh₃)ML]-complexes generally have distinct features that can be described in terms of the “*plane of nadir energy*”, a plane linking all points of minimum steric compression between the ligands. The generally observed orientation of PPh₃ involves a correlated feathering of the phenyl groups with the P–C_{ipso} bond of one phenyl group orientated near parallel to the nadir plane, and a meta carbon (C_m) of the other two phenyl groups orientated as near as possible to the nadir plane, orthogonal to the first. Although the orientation of PPh₃ in **6-trans**, [(CO)₄(PPh₃)W = C(OEt)2-furyl], deviates from this, DFT correctly calculated the unexpected and not generally observed PPh₃ orientation.

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1. Introduction

The electronic structure of the metal–carbon bond in carbene complexes determines the reactivity of the complex [1]. Fischer carbene complexes feature strong π-acceptors ligands at the metal centre and are electrophilic at the carbene carbon atom [2].

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Modification of the ligand sphere around the metal centre will alter the electronic properties of the complex and hence its reactivity. One of the applications of the Fischer carbenes is in the field of catalysis [3]. Fischer carbene complexes are known to transfer CR_2 moieties ($R = H$, alkyl, aryl, alkoxy, amino) in cyclopropanation and olefin metathesis reactions [4]. However, because they are coordinately and electronically saturated, these complexes do not normally initiate olefin metathesis. Only under thermal or photochemical activation, or in the presence of a co-catalyst can they initiate a metathesis reaction.

Phosphines have many applications in organometallic chemistry, specifically as ligands in homogenous catalysts [5]. Combining phosphines and carbenes in one complex may lead to synergy regarding the catalytic properties, as was the result for reactions with electrophiles [6] and photocarbonylation reactions [7]. In phosphine-substituted Fischer carbene complexes, the phosphine group is often the most bulky part of the molecule. In the case of triphenylphosphine-containing complexes, the conformation of the phenyl rings often contributes to the bulkiness of the complex. The most bulky part of the molecule frequently determines the shape and reactivity of the complex [8]. Therefore, knowledge of the preferred conformation of the phenyl rings in triphenylphosphine-containing complexes could provide important information to the development of catalysts, especially in stereoselective reactions.

This contribution presents the synthesis and characterization of novel ($M = Cr$ or Mo) and known ($M = W$) $[(CO)_4(PPh_3)M=C(OEt)R]$ complexes, $M = Cr$, $R = 2$ -thienyl (**1**), 2-furyl (**2**); $M = Mo$, $R = 2$ -thienyl (**3**), 2-furyl (**4**); $M = W$, $R = 2$ -thienyl (**5**), 2-furyl (**6**), focusing on the structure of three selected triphenylphosphine-substituted Fischer carbene complexes (**1-cis**, **4-cis** and **6-trans**) and the preferred orientation of triphenylphosphine in the complexes. In this study, we report the first structure of a *trans*-substituted phosphine carbene complex (**6-trans**).

2. Experimental

2.1. General

All reactions, unless otherwise noted, were performed under inert nitrogen or argon atmospheres using standard Schlenk techniques. All solvents were freshly distilled, dried, and collected under inert conditions, with the exception of toluene. Toluene was not dried but was used after nitrogen gas was bubbled through the solvent for 5–10 min. All other reagents were used directly. Column chromatography was carried out under inert nitrogen and argon atmospheres at $-10^\circ C$ using silica gel (particle size 0.063–0.200 mm) as the stationary phase. All percentage yields were calculated relative to the limiting reactant. All crystallizations were done using hexane/DCM diffusion methods. The reagents $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, butyllithium (1.6 M solution in hexane), furan, PPh_3 and other commercial reagents were used as purchased. NMR spectra were recorded on a Bruker ARX-300, Bruker Ultra Shield 400 Plus AVANCE III, and Bruker AVANCE 500 instruments. NMR spectra were recorded in $CDCl_3$, CD_2Cl_2 , or CD_3CN using deuterated solvent peaks as the internal references. IR spectra were recorded on a Perkin–Elmer Spectrum RXI FT-IR spectrophotometer. All spectra were recorded as KBr pellets, and only the vibration bands in the carbonyl stretching region (ca. 1500–2200 cm^{-1}) are reported. Mass spectra were recorded on a SYNAPT G2 HDMS instrument with the TOF-MS method with a sampling time of 4 min, by the direct infusion inlet method. The source was electron spray ionization. Commercial thiophene was purified [9] and triethyloxonium tetrafluoroborate [10], $[(CO)_5Cr=C(OEt)2$ -thienyl] (**1**) [11], $[(CO)_5Cr=C(OEt)2$ -furyl] (**2**) [11,12], $[(CO)_5$

$Mo=C(OEt)2$ -thienyl] (**3**), [13] $[(CO)_5W=C(OEt)2$ -thienyl] (**5**) [14], $[(CO)_5W=C(OEt)2$ -furyl] (**6**) [12], $[(CO)_4(PPh_3)W=C(OEt)2$ -thienyl] (**5**) [15] and $[(CO)_4(PPh_3)W=C(OEt)2$ -furyl] (**6**) [15] were prepared according to reported literature procedures. The synthesis and characterization data of **1–6**, as well as that of the novel precursor $[(CO)_5Mo=C(OEt)2$ -furyl], (**4**), of complex **4**, are reported below. The carbon atoms for NMR were assigned according to the numbering of Scheme 1.

2.2. Synthesis

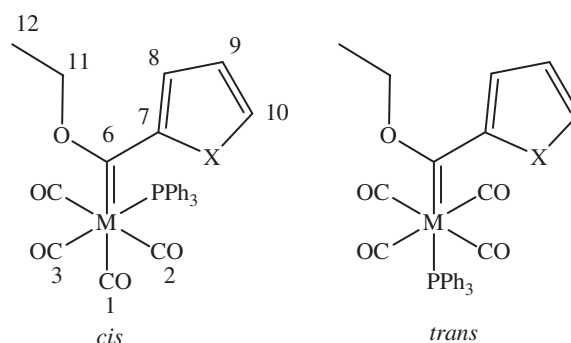
2.2.1. Synthesis of $[(CO)_5Mo=C(OEt)2$ -furyl], complex **4**

Furan (0.32 mL, 4.37 mmol) in 15 mL THF was cooled to $-35^\circ C$, and nBuLi (1.5 M, 3.13 mL, 4.70 mmol) was added dropwise, resulting in a pale yellow solution. The reaction was allowed to stir at $-35^\circ C$ for 40 min. $Mo(CO)_6$ (1.320 g, 4.99 mmol) was added and the reaction allowed to stir cold for a further 20 min (bright yellow solution), and then at RT for 1 h (dark red brown solution). The solvent was then removed, and a dark brown oil obtained. This product was dissolved in 30 mL of dichloromethane (DCM) and cooled to $-40^\circ C$. Et_3OBF_4 in DCM (0.2454 g/mL, 5 mL, 6.46 mmol) was added to the reaction mixture and allowed to stir for 30 min. The reaction was then allowed to stir at RT for 1 h, yielding a dark red–brown solution which was filtered through silica gel and rinsed off with DCM. A dark red–brown solid was obtained after solvent removal. The product was purified on silica gel with a hexane:DCM mixture (1:1).

$[(CO)_5Mo=C(OEt)2$ -furyl], (**4**): Yield 39.9%, red solid. 1H NMR ($CDCl_3$, ppm): 7.83 (dd, H10, 1.7, 0.8 Hz), δ 7.09 (dd, H8, 3.6, 0.8 Hz), 6.58 (dd, H9, 3.7, 1.7 Hz), 5.03 (q, H11, 7.1 Hz), 1.62 (t, H12, 7.0 Hz). ^{13}C NMR ($CDCl_3$, ppm): δ 301.1 (C6), 213.5 (s, CO_{trans}), 206.0 (t, CO_{cis}), 164.4 (C7), 150.0 (C10), 114.6 (C8), 113.2 (C9), 76.6 (C11), 15.2 (C12). IR (KBr, cm^{-1}): ν_{CO} 2068 (m), 1988 (m) 1942 (s) 1923 (vs).

2.2.2. Synthesis of complexes **1–6**

The relevant monocarbene complex **I–VI** (3.00 mmol) and PPh_3 (0.945 g, 3.60 mmol) were dissolved in 30 ml of toluene (red solution). This mixture was left to reflux for 8 h. The solvent was removed from the resulting dark brown solution to yield a dark brown residue. The crude product was purified on a silica gel column, cooled to $-10^\circ C$, using varying hexane:dichloromethane gradients. Unreacted monocarbene **I–VI** and two products were observed on TLC (thin layer chromatography). The two products



- 1-cis**: X = S, M = Cr
2-cis: X = O, M = Cr
3-cis: X = S, M = Mo
4-cis: X = O, M = Mo
5-cis; **5-trans**: X = S, M = W
6-cis; **6-trans**: X = O, M = W

Scheme 1. Cis- and trans- $[(CO)_4(PPh_3)M=C(OEt)R]$ complexes.

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