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$^{31}P\{^{1}H\}$NMR and carbonyl force constants of unsymmetrical bidentate phosphine complexes of group (VI) metal carbonyls

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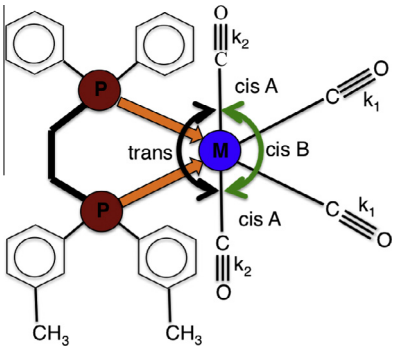
HIGHLIGHTS

- The labile nature of carbonyl ligands in the metal carbonyls allows us to prepare plethora of complexes.
- Metal carbonyl–phosphine complexes find applications as novel precursor materials for the synthesis of metal phosphides.
- Carbonyl force constants give valuable information on the electronic properties of complexes.
- Metal–ditertiary phosphine complexes recently find applications in tunable optical materials.
- Versatility of ligand substitutions offers many opportunities for developing novel bio-imaging reagents.

GRAPHICAL ABSTRACT



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ABSTRACT

In our present work we report synthesis of an unsymmetrical diphos ligand, 1-diphenylphosphino-2-di-*m*-tolylphosphinoethane and its coordinate complexes with group (VI) metal carbonyls such as $Cr(CO)_6$ $Mo(CO)_6$ and $W(CO)_6$. The synthesized ligand and its complexes have been completely characterized by elemental analyses, FTIR, ^{1}HNMR, $^{31}P\{^{1}H\}$NMR and FAB mass spectrometry methods. Special emphasis has been given to calculations of carbonyl force constants. Based on the spectroscopic evidences it has been confirmed that these metal carbonyl complexes with the ditertiary phosphine ligand showed *cis* geometry in their molecular structure.

Introduction

In organometallic chemistry, phosphines have been considered as important ligands as they have been widely used in organic reactions [1]. Phosphines are known to stabilize low oxidation states of metal centers and could be used to fine tune electronic and steric properties in their corresponding coordination complexes. There have been great many number of known transition-metal complexes that contain phosphine ligands which are either monodentate or multi-dentate and also with multiple substituents on phosphorus. The strong basicity of phosphines enhances their reactivity and stable complex formation toward electron deficient metal centers. The substituents present either at the phosphorus

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center or at the carbon backbone can alter electron donating or withdrawing property of the ligand. Nano-sized phosphine ligands containing bulky aromatic substituents have received great attention in recent years. Such bulky phosphines can be used as effective ligands in transition metal based reactions [2]. Phosphine ligands with bulky aromatic substituents showed excellent catalytic property in the alcohol oxidation [3], hydrosilylation [4] reactions with a suitable transition metal.

The group VI carbonyl complexes have been of interest for many years. These complexes play different roles depending on the substituents present on them. Molybdenum carbonyl complexes have been used as catalysts [5–7]. Metal carbonyls have been used for biological assays using the intense IR signal of the coordinated carbonyl ligand [8–10]. Recently metal carbonyl complexes have been studied as therapeutic CO-releasing molecules [11–13]. Interestingly metal carbonyl complexes with phosphines have been used to synthesize transition metal phosphides that have been used to prepare nanocrystalline spintronic materials [14]. Tris(trimethylsilyl)phosphine was used as a precursor for the synthesis of iron phosphide [15] and indium phosphide [16] nanoparticles. In view of these potential applications of metal carbonyl complexes of phosphines, we have been interested in synthesizing a ditertiary phosphine ligand that could find applications in the manufacturing of novel nanomaterial based devices. When phosphines are attached to aryl functional groups they open the possibility of multiple substituents with electron donating or withdrawing properties. The electronic and steric properties of this ligand could determine the available electron density around the metal center thereby alters its photophysical property. Transition metal carbonyl complexes with tunable photophysical properties have been a vital factor and determine their application in the development of optoelectronic or spintronic materials. Recently, Tsubomura and Nishikawa [17] synthesized and evaluated the photophysical properties of copper (I) complexes of 1,3-bis(diphenylphosphino)propane ligand. King and Kapoor [18] first synthesized an unsymmetrical diphos ligand, 1-diphenylphosphino-2-di-*m*-tolylphosphinoethane (m-t-dppe). However, complete spectroscopic characterization on this ligand was not carried out. Later Sadnani and coworkers [19] synthesized transition metal and group (VI) metal carbonyl complexes of m-t-dppe but reported only preliminary ^{1}HNMR chemical shift values of these complexes however, $^{31}P\{^{1}H\}$NMR characterization has not been done. In this present work, we have made an attempt to synthesize and characterize m-t-dppe complexes of chromium, molybdenum and tungsten hexacarbonyls. Special emphasis has been given to the $^{31}P\{^{1}H\}$NMR characterization and carbonyl force constant calculations.

Experimental section

The Infrared spectra of solid samples were recorded as KBr pellets in the region 4000–400 cm^{-1}. The elemental analyses, melting point measurements, ^{1}HNMR was recorded on a Bruker 400 MHz instrument using CD_2Cl_2 solvent, $^{31}P\{^{1}H\}$NMR was done using 85% H_3PO_4 as external standard. Chromium, molybdenum and tungsten hexacarbonyls were obtained from Sigma–Aldrich, US and used as such without further purification. The unsymmetrical ligand, 1-diphenylphosphino-2-di-*m*-tolylphosphinoethane (m-t-dppe) was synthesized as reported earlier [18].

Synthesis of cis-1-diphenylphosphino-2-di-m-tolyl phosphinoethane tetracarbonylchromium(0), cis-[Cr(CO)$_4${Ph$_2$P(CH$_2$)$_2$P(m-CH$_3$C$_6$H$_4$)$_2$}]

$Cr(CO)_6$ (120 mg, 0.54 mmol) and 1-diphenylphosphino-2-di-*m*-tolylphosphinoethane (232 mg, 0.54 mmol) were placed in a Schlenk tube and freshly distilled methylcyclohexane (15 mL) was added. The contents were stirred at room temperature for 1 h and then heated to reflux under nitrogen atmosphere at 100 °C for 30 h to give a clear yellow color solution. The solution was then cooled to room temperature and the solvent removed in high *vacuo* to give a yellow powder. It was purified by column chromatography on a short column of alumina using dichloromethane-petroleum ether (40–60 °C) as eluent. Slow evaporation of the solvent mixture under nitrogen, afforded the desired complex as pale yellow needles, which were isolated and dried under vacuum.

Yield: 182 mg, 56%; m.p. 161 °C (decomp.)

Anal. Calcd. for $C_{32}H_{28}O_4P_2Cr$: C, 65.09; H, 4.78; Found: C, 65.02; H, 4.54 FAB Mass Spectrum: (*m/z*) Calcd. for $C_{32}H_{28}O_4P_2Cr$ = 590.52, Obsd. = 591 $[M]^+$.

Synthesis of cis-1-diphenylphosphino-2-di-m-tolyl phosphinoethane tetracarbonylmolybdenum(0), cis-[Mo(CO)$_4${Ph$_2$P(CH$_2$)$_2$P(m-CH$_3$C$_6$H$_4$)$_2$}]

$Mo(CO)_6$ (120 mg, 0.45 mmol) and 1-diphenylphosphino-2-di-*m*-tolylphosphinoethane (194 mg, 0.45 mmol) were dissolved in freshly distilled methylcyclohexane (20 mL) in a Schlenk tube. The contents were heated to reflux under nitrogen atmosphere at 110 °C for 24 h resulting in the formation of a bright yellow solution. The solution was then cooled to room temperature and the solvent removed under high *vacuo* to give a yellow powder as the crude product. The product was washed several times with *n*-hexane and dried. The resultant product was then purified on a short column of alumina with dichloromethane-petroleum ether (40–60 °C) mixture (3:1). Slow evaporation of the solvent mixture gave the desired complex as yellow solid.

Yield: 178 mg, 61%; m.p. 147 °C (decomp.)

Anal. Calcd. for $C_{32}H_{28}O_4P_2Mo$: C, 60.58; H, 4.45; Found: C, 60.36; H, 4.23 FAB Mass Spectrum: (*m/z*) Calcd. for $C_{32}H_{28}O_4P_2Mo$ = 634.16, Obsd. = 634 $[M]^+$.

Synthesis of cis-1-diphenylphosphino-2-di-m-tolyl phosphinoethane tetracarbonyltungsten(0), cis-[W(CO)$_4${Ph$_2$P(CH$_2$)$_2$P(m-CH$_3$C$_6$H$_4$)$_2$}]

$W(CO)_6$ (150 mg, 0.43 mmol) and 1-diphenylphosphino-2-di-*m*-tolylphosphinoethane (182 mg, 0.43 mmol) were dissolved in distilled xylene (15 mL) in a Schlenk tube. The solution was heated to reflux under nitrogen atmosphere at 110 °C for 72 h to give a bright yellow solution. It was cooled to room temperature and the solvent was removed under high vacuo. The residue was washed several times with dry n-hexane and filtered through a G-3 funnel. The residue was then purified on a short column of alumina with a mixture of dichloromethane-petroleum ether (40–60 °C) as eluent. Removal of the solvents followed by recrystallization from dichloromethane-n-hexane gave a pale yellow solid.

Yield: 164 mg, 53%; m.p. 141 °C (decomp.)

Anal. Calcd. for $C_{32}H_{28}O_4P_2W$: C, 53.21; H, 3.9; Found: C, 53.34; H, 3.76 FAB Mass Spectrum: (*m/z*) Calcd. for $C_{32}H_{28}O_4P_2W$ = 722.38, Obsd. = 722 $[M]^+$.

Results and discussion

FTIR spectra

The IR spectra of the carbonyl complexes showed characteristic four $\nu_{C\equiv O}$ bands in the region (2100–1800 cm^{-1}). The four carbonyl stretching vibrations being distributed among the symmetry classes of the point group such as $\tau = 2A_1 + B_1 + B_2$. These vibrations may be considered as two pairs originating from (i)