Bimetallic Group 6 Tricarbonyls Containing Rigid Backbone Chelating Ligands Symmetrically Bridged by Bis(diphenylphosphino)alkane

Khalil J. Asali*, Mohammad El-khateeb, Ahmad Daraosheh

Chemistry Department, Jordan University of Science and Technology, Irbid, 22110, Jordan

Received on April 25, 2009 **Accepted on** June 4, 2009

Abstract

Bimetallic tricarbonyl complexes with chelating bis(diphenylphosphino)ethane or 1,10-phenanthroline bridged by bis(diphenylphosphino)alkane ligands of the type *fac*-[(L)M(CO)$_3$]$_2$(μ-dppa) (M = Mo *(1)*, W *(2)*; L = dppe, phen; dppa = dppe *(a)*, dppb *(b)*, dpph *(c)*, dppo *(d)*, dppd *(e)*) were prepared by the reaction of the labile tricarbonyl complexes *fac*-(L)M(CO)$_3$(py) with the desired dppa which acts as a bridging ligand. These complexes were characterized by FT-IR, ^{31}P and ^{1}H NMR spectroscopies and elemental analysis. A brief study of the thermodynamic stability of some of these complexes in chlorinated hydrocarbons at ambient temperatures was conducted employing FT-IR spectroscopy. All complexes are remarkably stable in solution for a prolonged period of time and show no *fac-mer* isomerization under conditions employed during this study.

Keywords: Metal carbonyls; Molybdenum; Tungsten; Bimetallic; Bridging bisphosphines.

Introduction

Complexes containing two metal centers of small proximity have attracted much attention in recent years based on the idea that the concerted effects of two metals should result in novel reactions useful in stoichiometric synthesis and catalysis [1-3]. A series of homonuclear and heteronuclear bimetallic compounds of the general formula (CO)$_5$M(μ-L-L)M'(CO)$_5$, (M, M' = Cr, Mo, W; L-L = 4,4'-bipyridine, 1,2-bis(4-pyridyl)ethane, 1,2-bis(4-pyridyl)ethylene, pyrazine, 4,4'-dipyridylbutadiyne, 1,4-bis(4'-pyridylethynyl)benzene) have been reported [4-12].

Another class of homobimetallic carbonyl compounds employing the bridging ligands bis(diphenylphosphino)alkane (dppa) and/or dithiaalkane (DTA) such as (CO)$_4$(L')M(μ-L-L)M'(CO)$_4$(L') (M= Mo, W; L-L = dppa, DTA; L' = CO, pip) have been prepared, characterized and kinetically studied by us [13-16]. Binuclear metal tetracarbonyl compounds doubly-bridged by these dppa and/or DTA ligands have also been obtained by direct one-pot reactions between the labile M(CO)$_4$(pip)$_2$ complex and the corresponding dppa or DTA ligands [17].

We have recently reported the synthesis of bimetallic carbonyl complexes triply-bridged by dppa ligands of the type [M(CO)$_3$]$_2$[μ-dppa]$_3$ (M= Cr, Mo, W), which were

* Corresponding author: E-mail: *asali@just.edu.jo*

obtained by the reaction of the labile complex $M(CO)_3(Me_3tach)$ with dppa ligand (Me_3tach = 1,3,5-trimethyl-1,3,5-triazacyclohexane) [18]. Bimetallic tricarbonyl complexes containing both chelating 1,10-phenanthroline and a bridging PNP bisphosphine ligand (PNP = bis(diphenylphosphinoethyl)ethylamine) of the general formula *fac*-$[(phen)(CO)_3Mo]_2(\mu\text{-PNP})$ in which bridging occurs through the two phosphorus atoms, while the N-atom of the PNP ligand remains uncoordinated, are also known [19].

It has been observed earlier that the triply bridged complexes of the type $[M(CO)_3]_2[\mu\text{-dppa}]_3$ (M = Cr, Mo) were not highly stable in solution and may undergo excessive decomposition upon standing in solution for a prolonged period of time [18]. It is expected that inclusion of a chelating ligand with rigid backbone on each metal carbonyl fragment may increase the thermal stability of these complexes. In this study, we report a series of bimetallic molybdenum and tungsten complexes containing chelating bis(diphenylphosphino)ethane or 1,10-phenanthroline and a bridging bis(diphenylphosphino)alkane. The thermal stability of these new complexes in solution is also discussed.

Experimental

Materials and Methods

All reactions were performed under nitrogen atmosphere using schlenk techniques. Dichloromethane and 1,2-dichloroethane were dried and distilled over P_2O_5. Hexane, pentane and THF were dried and distilled over sodium and benzophenone. Toluene, xylene, pyridine and absolute methanol were used without further purification. The following chemicals were used as received: (Aldrich, Acros) tungsten hexacarbonyl, molybdenum hexacarbonyl, dibromoalkanes, mesitylene, triphenylphosphine, and 1,10-phenanthroline. The complexes: *cis*-$(L)M(CO)_4$ and *fac*-$(L)M(CO)_3(py)$ (M = Mo, W; L = dppe, phen; py = pyridine) [20, 21] and the dppa [22, 23] were prepared according to literature procedures. Infrared spectra were recorded on a Nicolet impact 410 FT-IR spectrometer. ^1H and ^{31}P NMR spectra were recorded on a Bruker AVANCE 400 MHz spectrometer and on a Varian Mercury-400BB 400 MHz. Elemental analyses were performed by M-H-W laboratories, Phoenix, Arizona, USA and the Institute of Chemistry, University of Podlasie, Poland.

General procedure for the preparation of fac-[(η^2-dppe)Mo(CO)$_3$]$_2$(μ-dppa) complexes (1)

A dichloromethane solution (25 mL) containing a mixture of dppa (0.15 mmol) and *fac*-$(\eta^2\text{-dppe})Mo(CO)_3(py)$ (0.20 g, 0.30 mmol) was stirred for about 1.5 hours at room temperature. The resulting solution was filtered over Celite. The solvent was removed under reduced pressure at room temperature. The solid residue was collected by suction filtration and was washed several times with hot hexane to remove any unreacted dppa. The resulting pale yellow powder was recrystallized at room temperature form CH_2Cl_2/hexane (1:3 v:v) mixture.

fac-[(η²-dppe)Mo(CO)₃]₂(μ-dppe) (1a): Yield = 78%. M.p = 195-197ºC. Anal Calcd for $C_{84}H_{72}O_6P_6Mo_2$: C, 64.87; H, 4.67%. Found: C, 64.24; H, 5.02%. I.R (CH_2Cl_2, cm^{-1}): ν_{CO}: 1938 (s), 1843 (s). ^{31}P-{^1H} NMR ($CDCl_3$), **δ** ppm: 48.3, η²-dppe; 29.9, μ-dppe. ^1H NMR ($CDCl_3$), **δ** ppm: 2.50-2.66 (4H, η²-dppe); 2.36-2.40 (4H, μ-dppe); 6.96-7.85 (40H, Ph).

fac-[(η²-dppe)Mo(CO)₃]₂(μ-dppb) (1b): Yield = 75%. M.p = 184-185ºC. Anal Calcd for $C_{86}H_{76}O_6P_6Mo_2$: C, 65.24; H, 4.84%. Found: C, 64.78; H, 5.18%. IR (CH_2Cl_2, cm^{-1}): ν_{CO}: 1937 (s), 1841 (s). ^{31}P-{^1H} NMR ($CDCl_3$), **δ** ppm: 47.8, η²-dppe; 27.4, μ-dppb. ^1H NMR ($CDCl_3$), **δ** ppm: 2.40-2.52 (4H, η²-dppe); 1.35-1.54 (4H, CH_2); 2.10-2.32 (4H, CH_2Ph_2); 7.02-7.68 (40H, Ph).

fac-[(η²-dppe)Mo(CO)₃]₂(μ-dpph) (1c): Yield = 71%. M.p = 180-183ºC (dec.). Anal Calcd for $C_{88}H_{80}O_6P_6Mo_2$: C, 65.60; H, 5.00%. Found: C, 65.44; H, 5.22%. I.R (CH_2Cl_2, cm^{-1}) ν_{CO}: 1938 (s), 1841 (s). ^{31}P-{^1H} NMR ($CDCl_3$), **δ** ppm: 49.3, η²-dppe; 28.3, μ-dpph. ^1H NMR ($CDCl_3$), **δ** ppm: 2.25-2.44 (4H, η²-dppe); 1.12-2.24 (8H, CH_2); 2.50-2.74 (4H, CH_2Ph_2); 7.05-7.70 (40H, Ph).

fac-[(η²-dppe)Mo(CO)₃]₂(μ-dppo) (1d): Yield = 76%. M.p = 161-163ºC (dec.). Anal Calcd for $C_{90}H_{84}O_6P_6Mo_2$: C, 65.94; H, 5.16%. Found: C, 65.83; H, 5.30%. I.R. (CH_2Cl_2, cm^{-1}): ν_{CO}: 1937 (s), 1842 (s). ^{31}P-{^1H} NMR ($CDCl_3$), **δ** ppm: 49.8, η²-dppe; 31.7, μ-dppo. ^1H NMR (CDCl3, **δ** ppm: 2.10-2.22 (4H, η²-dppe); 1.20-1.46 (12H, CH_2); 2.38-2.62 (4H, CH_2Ph_2); 7.00-7.84 (40H, Ph).

fac-[(η²-dppe)Mo(CO)₃]₂(μ-dppd) (1e): Yield = 68%. M.p = 151-152ºC (dec.). Anal Calcd for $C_{92}H_{88}O_6P_6Mo_2$: C, 66.27; H, 5.32%. Found: C, 66.42; H, 5.42%. I.R. (CH_2Cl_2, cm^{-1}): ν_{CO}: 1938 (s), 1840 (s). ^{31}P-{^1H}NMR ($CDCl_3$), **δ** ppm: 46.0, η²-dppe; 30.1, μ-dppd. ^1H NMR (CDCl3), **δ** ppm: 2.22-2.30 (4H, η²-dppe); 1.26-1.62 (16H, CH_2); 2.46-2.65 (4H, CH_2Ph_2); 7.20-7.74 (40H, Ph).

General procedure for the preparation of fac-[(η²-dppe)W(CO)₃]₂(μ-dppa) complexes (2)

A 1,2-dichloroethane solution (25 mL) containing a mixture of dppa (0.14 mmol) and *fac*-(η²-dppe)W(CO)₃(py) (0.21 g, 0.28 mmol) was stirred for about 3 hours at ~ 50°C under nitrogen atmosphere. The work up is similar to that of complexes *(1)*.

fac-[(η²-dppe)W(CO)₃]₂(μ-dppe) (2a): Yield = 79%. M.p = 175-178ºC (dec.). Anal Calcd for $C_{84}H_{72}O_6P_6W_2$: C, 58.28; H, 4.19%. Found: C, 57.82; H, 4.52%. IR (CH_2Cl_2, cm^{-1}): ν_{CO}: 1933 (s), 1834 (s). ^{31}P-{^1H}MR ($CDCl_3$), **δ** ppm: 36.4, *J*(WP) 228 Hz, η²-dppe; 7.1, *J*(WP) 242 Hz, μ-dppe. ^1H NMR ($CDCl_3$), **δ** ppm: 2.48-2.56 (4H, η²-dppe); 2.30-2.38 (4H, μ-dppe); 7.323-7.55 (40H, Ph).

fac-[(η²-dppe)W(CO)₃]₂(μ-dppb) (2b): Yield = 76%. M.p = 180-184ºC (dec.). Anal Calcd for $C_{86}H_{76}O_6P_6W_2$: C, 58.72; H, 4.35%. Found: C, 58.34; H, 4.63%. IR (CH_2Cl_2, cm^{-1}):

v_{CO}: 1932 (s), 1834 (s). ^{31}P-{^{1}H} NMR ($CDCl_3$), **δ** ppm: 37.2, *J*(WP) 228 Hz, η^2-dppe; 11.3, *J*(WP) 238 Hz, μ-dppb. ^{1}H NMR ($CDCl_3$), **δ** ppm: 2.52-2.55 (4H, η^2-dppe); 1.25-1.42 (4H, CH_2); 2.15-2.38 (4H, CH_2Ph_2); 7.43-7.60 (40H, Ph).

fac-[(η^2-dppe)W(CO)$_3$]$_2$(μ-dpph) (2c): Yield = 72%. M.p = 188-192ºC (dec.). Anal Calcd for $C_{88}H_{80}O_6P_6W_2$: C, 59.14; H, 4.51%. Found: C, 58.88; H, 4.45%. IR (CH_2Cl_2, cm^{-1}): v_{CO}: 1932 (s), 1833 (s). ^{31}P-{^{1}H} NMR ($CDCl_3$), **δ** ppm: 36.1 *J*(WP) 228 Hz, η^2-dppe; 10.0, *J*(WP) 242 Hz, μ-dpph. ^{1}H NMR ($CDCl_3$), **δ** ppm: 2.28-2.36 (4H, η^2-dppe); 1.15-2.32 (8H, CH_2); 2.55-2.68 (4H, CH_2Ph_2); 7.25-7.54 (40H, Ph).

fac-[(η^2-dppe)W(CO)$_3$]$_2$(μ-dppo) (2d): Yield = 76%. M.p = 196ºC (dec.). Anal Calcd for $C_{90}H_{84}O_6P_6W_2$: C, 59.55; H, 4.66%. Found: C, 58.91; H, 4.54%. IR (CH_2Cl_2, cm^{-1}): v_{CO}: 1932 (s), 1835 (s). ^{31}P-{^{1}H} NMR ($CDCl_3$), **δ** ppm: 33.9, *J*(WP) 232 Hz, η^2-dppe; 7.0, *J*(WP) 236 Hz, μ-dppo. ^{1}H NMR ($CDCl_3$), **δ** ppm: 2.46-2.52 (4H, η^2-dppe); 1.24-1.44 (12H, CH_2); 2.38-2.62 (4H, CH_2Ph_2); 7.66-7.84 (40H, Ph).

fac-[(η^2-dppe)W(CO)$_3$]$_2$(μ-dppd) (2e): Yield = 68%. M.p = 202ºC (dec.). Anal Calcd for $C_{92}H_{88}O_6P_6W_2$: C, 59.95; H, 4.81%. Found: C, 59.78; H, 5.06%. IR (CH_2Cl_2, cm^{-1}): v_{CO}: 1932 (s), 1834 (s). ^{31}P-{^{1}H} NMR ($CDCl_3$), **δ** ppm: 37.2, *J*(WP) 235 Hz, η^2-dppe; 11.1, *J*(WP) 242 Hz, μ-dppd. ^{1}H NMR ($CDCl_3$), **δ** ppm: 2.28-2.42 (4H, η^2-dppe); 1.26-1.62 (16H, CH_2); 2.48-2.75 (4H, CH_2Ph_2); 7.42-7.64 (40H, Ph).

General procedure for the preparation of fac-[(phen)Mo(CO)$_3$]$_2$(μ-dppa) complexes, (3)

A dichloromethane solution (30 mL) containing a mixture of dppa (0.23 mmol) and *fac*-(1,10-phenanthroline)Mo(CO)$_3$(py) (0.20 g, 0.46 mmol) was stirred for about 1.5 hours at room temperature under nitrogen atmosphere. The resulting solution was filtered over Celite. The solvent was removed under reduced pressure at room temperature. The solid residue was collected by suction filtration and was washed several times with hot hexane to remove any unreacted dppa ligands. The resulting dark-violet powder was recrystallized at room temperature from CH_2Cl_2/hexane (v:v 1:3) mixture. The following complexes were prepared according to this procedure:

fac-[(phen)Mo(CO)$_3$]$_2$(μ-dppe) (3a): Yield = 84%. M.p = 245-246ºC. Anal Calcd for $C_{56}H_{40}O_6P_2N_4Mo_2$: C, 60.12; H, 3.60; N, 5.01%. Found: C, 59.75; H, 3.46; N, 5.12%. IR (CH_2Cl_2, cm^{-1}): v_{CO}: 1912 (s), 1816 (s, b), 1786 (s, b). ^{31}P-{^{1}H} NMR ($CDCl_3$), **δ** ppm: 31.8, μ-dppe. ^{1}H NMR ($CDCl_3$), **δ** ppm: 6.85-0-7.20 (20H, ph); 7.64-9.1 (16H, phen); 2.42-2.26 (4H, CH_2Ph).

fac-[(phen)Mo(CO)$_3$]$_2$(μ-dppb) (3b): Yield = 80%. M.p = 238-242ºC. Anal Calcd for $C_{58}H_{44}O_6P_2N_4Mo_2$: C, 60.74; H, 3.87; N, 4.89%. Found: C, 60.37; H, 3.99; N, 5.00%. IR (CH_2Cl_2, cm^{-1}): v_{CO}: 1912 (s), 1808 (s ,b), 1786 (s ,b). ^{31}P-{^{1}H} NMR ($CDCl_3$), **δ** ppm: 27.2, μ-dppb. ^{1}H NMR ($CDCl_3$), **δ** ppm: 6.90-0-7.25 (20H, ph); 7.64-9.1 (16H, phen), 1.35-1.42 (4H, CH_2); 2.28-2.36 (4H, CH_2Ph).

fac-[(phen)Mo(CO)$_3$]$_2$(μ-dpph) (3c): Yield = 72%. M.p = 218-222ºC. Anal Calcd for $C_{60}H_{48}O_6P_2N_4Mo_2$.: C, 61.34; H, 4.12; N, 4.77%. Found: C, 60.95; H, 4.10; N, 4.90%. IR (CH_2Cl_2, cm^{-1}): ν_{CO}: 1912 (s), 1814 (s, b), 1783 (s, b). ^{31}P-{^1H} NMR ($CDCl_3$), **δ** ppm: 28.1, μ-dpph. ^1H NMR ($CDCl_3$), **δ** ppm: 6.80-7.40 (20H, ph), 7.64-9.1 (16H, phen), 1.26-1.48 (8H, CH_2); 2.40-2.56 (4H, CH_2Ph).

fac-[(phen)Mo(CO)$_3$]$_2$(μ-dppo) (3d): Yield = 66%. M.p = 196-197ºC. Anal Calcd for $C_{62}H_{52}O_6P_2N_4Mo_2$: C, 61.90; H, 4.36; N, 4.66%. Found: C, 61.95; H, 4.18; N, 4.86%. IR (CH_2Cl_2, cm^{-1}): ν_{CO}: 1912 (s), 1813 (s, b), 1786 (s, b). ^{31}P-{^1H} NMR ($CDCl_3$), **δ** ppm: 30.3, μ-dppo. ^1H NMR ($CDCl_3$), **δ** ppm: 6.65-0-7.38 (20H, ph), 7.64-9.1 (16H, phen), 1.30-1.42 (12H, CH_2); 2.48-2.60 (4H, CH_2Ph).

fac-[(phen)Mo(CO)$_3$]$_2$(μ-dppd) (3e): Yield = 68%. M.p = 173-174ºC. Anal Calcd for $C_{64}H_{56}O_6P_2N_4Mo_2$: C, 62.45; H, 4.59; N, 4.55%. Found: C, 62.32; H, 4.71; N, 4.38%. IR (CH_2Cl_2, cm^{-1}): ν_{CO}: 1912 (s), 1813 (s, b), 1786 (s, b). ^{31}P-{^1H} NMR ($CDCl_3$), **δ** ppm: 31.4, μ-dppd. ^1H NMR ($CDCl_3$), **δ** ppm: 7.00-0-7.44 (20H, ph), 7.82-9.35 (16H, phen), 1.20-1.50 (16H, CH_2); 2.40-2.52 (4H, CH_2Ph).

General procedure for the preparation of fac-[(phen)W(CO)$_3$]$_2$(μ-dppa) complexes, (4)

A 1,2-dichloroethane solution (30 mL) containing a mixture of dppa ligand (0.19 mmol) and *fac*-(1,10-phenanthroline)$W(CO)_3$(py) (0.20 g, 0.38 mmol) was stirred for about 3 hours at ~ 50°C under nitrogen atmosphere. The work up is similar to that of complexes *(3)*. The following complexes were prepared according to this procedure:

fac-[(phen)W(CO)$_3$]$_2$(μ-dppe) (4a): Yield = 81%. M.p = 256-260ºC (dec.). Anal Calcd for $C_{56}H_{40}O_6P_2N_4W_2$: C, 51.96; H, 3.11; N, 4.33%. Found: C, 51.52; H, 2.99; N, 4.08%. IR (CH_2Cl_2, cm^{-1}): ν_{CO}: 1905 (s), 1811 (s, b), 1775 (s, b). ^{31}P-{^1H} NMR ($CDCl_3$), **δ** ppm:10.8, *J*(WP) 244 Hz. ^1H NMR ($CDCl_3$), **δ** ppm: 6.92-7.40 (20H, ph); 7.54-9.22 (16H, phen); 2.12-2.26 (4H, CH_2Ph).

fac-[(phen)W(CO)$_3$]$_2$(μ-dppb) (4b): Yield = 80%. M.p = 233-235ºC (dec.). Anal Calcd for $C_{58}H_{44}O_6P_2N_4W_2$: C, 52.67; H, 3.35; N, 4.24%. Found: C, 52.18; H, 3.13; N, 4.50%. IR (CH_2Cl_2, cm^{-1}): ν_{CO}: 1905 (s), 1810 (s, b), 1776 (s, b). ^{31}P-{^1H} NMR ($CDCl_3$), **δ** ppm: 11.6, *J*(WP) 240 Hz. ^1H NMR ($CDCl_3$), **δ** ppm: 6.80-0-7.35 (20H, ph); 7.88-9.28 (16H, phen), 1.38-1.40 (4H, CH_2); 2.14-2.40 (4H, CH_2Ph).

fac-[(phen)W(CO)$_3$]$_2$(μ-dpph) (4c): Yield = 72%. M.p = 218-220ºC (dec.). Anal Calcd for $C_{60}H_{48}O_6P_2N_4W_2$: C, 53.35; H, 3.58; N, 4.15%. Found: C, 52.88; H, 3.29; N, 4.55%. IR (CH_2Cl_2, cm^{-1}): ν_{CO}: 1904 (s), 1809 (s, b), 1776 (s, b). ^{31}P-{^1H} NMR ($CDCl_3$), **δ** ppm: 9.9, *J*(WP) 238 Hz. ^1H NMR ($CDCl_3$), **δ** ppm: 6.98-0-7.40 (20H, ph); 7.90-9.32 (16H, phen), 1.29-1.46 (4H, CH_2); 2.24-2.36 (4H, CH_2Ph).

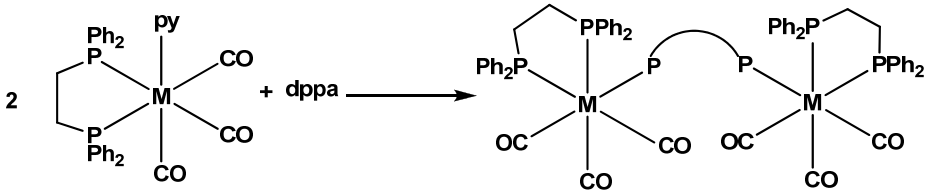
fac-[(phen)W(CO)$_3$]$_2$(μ-dppo) (4d): Yield = 68%. M.p = 220-224ºC (dec.). Anal Calcd for $C_{62}H_{52}O_6P_2N_4W_2$: C, 54.01; H, 3.80; N, 4.06%. Found: C, 53.62; H, 3.85; N, 4.41%. IR (CH_2Cl_2, cm^{-1}): v_{CO}: 1905 (s), 1807 (s, b), 1781 (s, b). ^{31}P-{^1H} NMR ($CDCl_3$), **δ** ppm: 11.8, *J*(WP) 246 Hz. ^1H NMR ($CDCl_3$), **δ** ppm: 7.05-0-7.45 (20H, ph); 7.86-9.38 (16H, phen), 1.33-1.52 (4H, CH_2); 2.10-2.31 (4H, CH_2Ph).

fac-[(phen)W(CO)$_3$]$_2$(μ-dppd) (4e): Yield = 78%. M.p = 174-175°C. Anal Calcd for $C_{64}H_{56}O_6P_2N_4W_2$: C, 54.64; H, 4.01; N, 3.98%. Found: C, 55.14; H, 3.85; N, 4.27%. IR (CH_2Cl_2, cm^{-1}): v_{CO}: 1905 (s), 1805 (s, b), 1783 (s, b). ^{31}P-{^1H} NMR ($CDCl_3$), **δ** ppm: 11.4, *J*(WP) 234 Hz. ^1H NMR ($CDCl_3$), **δ** ppm: 6.76-0-7.25 (20H, ph); 7.62-9.14 (16H, phen), 1.41-1.520 (4H, CH_2); 2.22-2.38 (4H, CH_2Ph).

Results and discussion

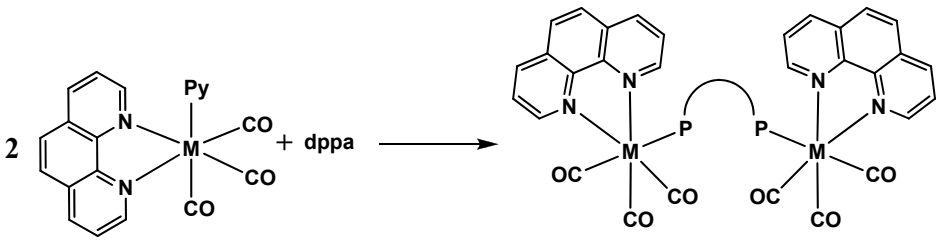
Synthesis of complexes

Symmetrically bridged dimers, *fac*-[(η^2-dppe)M(CO)$_3$)]$_2$(μ-dppa) [M = Mo *(1)*, W *(2)*, dppa = dppe *(a),* dppb *(b)*, dpph *(c)*, dppo *(d)*, dppd *(e)*] and *fac*-[(phen)M(CO)$_3$]$_2$(μ-dppa) [M = Mo *(3)*, W *(4)*], were prepared in good yields by reacting *fac*-(dppe)M(CO)$_3$(py) with dppa (2:1 molar ratio) (M= Mo, room temperature, dichloromethane solvent; M = W, 50°C 1,2-dichloroethane solvent) under nitrogen atmosphere as shown in equations 1 and 2.



M= Mo *(1)*, W *(2)*

dppa = P⌒P = dppe *(a)*, dppb *(b)*, dpph *(c),* dppo *(d)*, dppd *(e)*



M= Mo *(3)*, W *(4)*

dppa = P⌒P = dppe *(a)*, dppb *(b)*, dpph *(c),* dppo *(d)*, dppd *(e)*

Complexes *(1)* and *(2)* are pale-yellow while complexes *(3)* and *(4)* are dark-violet. All these complexes are air stable as solids and in solution. They are soluble in most polar-organic solvents such as CH_2Cl_2, THF and 1,2-dichloroethane. Complexes

(1)-(4) were characterized by FT-IR, ^{31}P, ^{1}H NMR spectroscopies and elemental analyses.

The IR spectra of *(1)* and *(2)* complexes, with an expected *pseudo-*C_{3v} local symmetry, exhibit two carbonyl stretching frequencies (A_1 and E modes) in the CO-stretching region for the two equivalent sets of three carbonyls on each metal center. These bands are found at ca. 1937 and 1840, cm^{-1} for *(1a-1e)*; 1932 and 1834 cm^{-1} for *(2a-2e)*. Taking into consideration that the local symmetry of the CO groups in *(3)* and *(4)* is reduced to C_s point group, since dppa and the chelating phen ligand have different bonding properties, the E mode will undergo splitting to two modes with 2A' symmetries, and three carbonyl stretching frequencies should be observed [24]. These bands are found at ca.1912, 1808, and 1783 cm^{-1} for *(3a-3e)*; 1905, 1811, and 1780 cm^{-1} for *(4a-4e)*. The CO-stretching frequencies in complexes *(3)* and *(4)* appear at lower values compared to those of *(1)* and *(2)*, which could be attributed to better σ-electrons donation but weaker π–electrons accepting ability of phen ligand compared to that of dppe, which results in higher electron density on the metal (Mo, W) and thus lower CO-stretching frequencies. The difference in ligand chain length for different dppa ligands does not seem to affect the carbonyl stretching frequencies in the complexes *(1)-(4)* to a considerable extent.

The ^{31}P NMR chemical shifts for the complexes *(1)-(4)* have been determined and unambiguously revealed that the bridging bisphosphine and the chelated dppe or phen ligands in these complexes are facial to each other rather than a mixture of facial and meridional isomers. This conclusion was confirmed from the number of equivalent signals in the ^{31}P NMR spectra of these complexes. The ^{31}P NMR spectra for the [(η^2-dppe)$Mo(CO)_3]_2$(μ-dppa) complexes *(1)* display two sets of resonances, one set for the two equivalent phosphorous of the chelating dppe ligand in the range of 46.0-49.8 ppm, and the other set for the bridging dppa ligands in the range of 27.4-31.7 ppm. ^{31}P NMR spectra for the *fac*-[(η^2-dppe)$W(CO)_3]_2$(μ-dppa) complexes *(2)* exhibited also two sets of phosphorous signals, one for the two equivalent P-atoms of the chelating dppe ligand in the range of 33.9-37.2 ppm with a ^{183}W satellites, with J(^{183}W-^{31}P) of 228-235 Hz, and the other set for the two equivalent P-atoms of the bridging dppa ligands in the range of 7.0-11.3 ppm with a ^{183}W satellites of J(^{183}W-^{31}P) 236-242 Hz. ^{31}P NMR spectra for the *fac*-[(phen)$Mo(CO)_3]_2$(μ-dppa) complexes *(3)* exhibited one resonance signal for the two equivalent P-atoms for the bridging dppa at 27.2-31.8 ppm. The corresponding *fac*-[(phen)$W(CO)_3]_2$(μ-dppa) complexes *(4)* also exhibited one resonance signal for the two equivalent P-atoms in the dppa bridging ligands at 9.9-11.8 ppm with a J(WP) in the range of 234-244 Hz. In general, the ^{31}P resonances of the chelating dppe and the bridging dppa in complexes *(1)-(4)* are shifted downfield compared to the ^{31}P resonances of the free uncoordinated dppa ligands. The values of $\Delta\delta_C$ (= $\delta_{(chelating\ dppe)} - \delta_{(uncoordinated\ dppe)}$ and $\Delta\delta_B$ (= $\delta_{(bridging\ dppa)} - \delta_{(uncoordinated\ dppa)}$), which represent these downfield shifts are given in Table 1. These coordination shifts vary in

the order Mo > W which is in agreement with results obtained for similar group 6 metal carbonyls containing bisphosphines as bridging or chelating ligands [25-28]. The ^{1}H NMR spectra of the complexes *(1)-(4)* exhibit proton chemical shifts in the expected regions, and were comparable to the chemical shifts of the corresponding dppa and phen free and chelating ligands.

Table 1. Coordination shifts of the ^{31}P NMR resonances for the complexes (1)-(4)

Complex		$\Delta\delta_C$ [a] (ppm)	$\Delta\delta_B$ [b] (ppm)
fac-[(η^2-dppe)Mo(CO)$_3$]$_2$(μ-dppe)	**(1a)**	60.3	41.9
fac-[(η^2-dppe)Mo(CO)$_3$]$_2$(μ-dppb)	**(1b)**	59.8	42.9
fac-[(η^2-dppe)Mo(CO)$_3$]$_2$(μ-dpph)	**(1c)**	61.3	43.24
fac-[(η^2-dppe)Mo(CO)$_3$]$_2$(μ-dppo)	**(1d)**	61.8	46.6
fac-[(η^2-dppe)Mo(CO)$_3$]$_2$(μ-dppd)	**(1e)**	58.0	43.5
fac-[(η^2-dppe)W(CO)$_3$]$_2$(μ-dppe)	**(2a)**	48.4	19.1
fac-[(η^2-dppe)W(CO)$_3$]$_2$(μ-dppb)	**(2b)**	49.2	26.8
fac-[(η^2-dppe)W(CO)$_3$]$_2$(μ-dpph)	**(2c)**	48.1	25.0
fac-[(η^2-dppe)W(CO)$_3$]$_2$(μ-dppo)	**(2d)**	45.9	21.9
fac-[(η^2-dppe)W(CO)$_3$]$_2$(μ-dppd)	**(2e)**	49.2	24.5
fac-[(phen)Mo(CO)$_3$]$_2$(μ-dppe)	**(3a)**	-----	43.8
fac-[(phen)Mo(CO)$_3$]$_2$(μ-dppb)	**(3b)**	-----	42.7
fac-[(phen)Mo(CO)$_3$]$_2$(μ-dpph)	**(3c)**	-----	43.0
fac-[(phen)Mo(CO)$_3$]$_2$(μ-dppo)	**(3d)**	-----	45.2
fac-[(phen)Mo(CO)$_3$]$_2$(μ-dppd)	**(3e)**	-----	44.7
fac-[(phen)W(CO)$_3$]$_2$(μ-dppe)	**(4a)**	-----	22.8
fac-[(phen)W(CO)$_3$]$_2$(μ-dppb)	**(4b)**	-----	27.1
fac-[(phen)W(CO)$_3$]$_2$(μ-dpph)	**(4c)**	-----	24.9
fac-[(phen)W(CO)$_3$]$_2$(μ-dppo)	**(4d)**	-----	26.7
fac-[(phen)W(CO)$_3$]$_2$(μ-dppd)	**(4e)**	-----	24.8

[a] $\Delta\delta_C = \delta_{(\text{chelating dppe})} - \delta_{(\text{uncoordinated dppe})}$; $\Delta\delta_B = \delta_{(\text{bridging dppa})} - \delta_{(\text{uncoordinated dppa})}$.

[a,b] ^{31}P δ uncoordinated ligands (ppm): dppe, -12.0; dppb, -15.5; dpph, -15.0; dppo, -14.9; dppd, -13.4.

Thermodynamic stability of (1)-(4) complexes in chlorinated hydrocarbon solutions

Complexes *(1)-(4)* contain a chelating bidentate ligands (dppa or phen) in the basal plane of these octahedral compounds, and thus it is expected that ligand scrambling will be highly hindered and a considerable stability of these complexes should result. In fact, these complexes have shown remarkable stability in CH_2Cl_2 solution and resisted decomposition or *fac-mer* isomerization at ambient temperatures over a period of ~ 24 hours, as indicated by the invariance of the IR spectra in the

carbonyl stretching region. Besides, complexes *(1)-(4)* are thermally more stable than bimetallic carbonyl complexes triply bridged by dppa ligands reported earlier [18]. This extra stability might be attributed to the presence of a rigid backbone such as dppe or phen chelating ligands in the skeleton of these complexes. It is also important to mention that such thermal stability is highly significant especially if some of these complexes are used in some environmental processes including application as solvatochromic "molecular grid" materials [29, 30], or as models for some homogeneous catalytic reactions such as olefin hydrogenation, polymerization and hydroformylation [31-37].

Conclusion

The results of this study show that bimetallic group 6 carbonyls containing chelating bis(diphenylphosphino)ethane or 1,10-phenanthroline and bridging dppa can be obtained by reactions of *fac*-(L)M$(CO)_3$(py) (L = dppe, phen; M = Mo, W) with the desired dppa (2:1 molar ratios). These complexes are remarkably stable in solution for a prolonged period of time and show no *fac-mer* isomerization under the conditions employed in this study.

Acknowledgements

The authors thank the Deanship of Scientific Research, Jordan University of Science & Technology for financial support, grant number 111/2005. The authors are also grateful to Prof. Stanislaw Ostrowski, Institute of Chemistry, University of Podlasie, Poland for ^1H, ^{31}P NMR spectra and elemental analysis.

References

[1] Darensbourg, D.J.; Klausmayer, K.K.; Reibenspies, J.H., *Inorg. Chem.*, 1995, 34, 4933.
[2] Zhuang, B.; Sum, H.; Pan, G.; He, L.; Wei, Q.; Zhou, Z.; Peng, S.; Wu, K., *J. Organomet. Chem.*, 2001, 640, 127.
[3] Pan, G.; Zhuang, B.; He, L.; Lu, J., *J. Organomet. Chem.*, 1999, 580, 313.
[4] Wong, W.Y.; Cheung, S.H.; Lee, S.M.; Leung, S.Y., *J. Organomet. Chem.*, 2000, 596, 36.
[5] Lees, A.A.; Fobare, J.M; Mattimore, E.F., *Inorg. Chem.*, 1984, 23, 2709.
[6] Zulu, M.M.; Lees, A.J., *Inorg. Chem.*, 1988, 27, 1139.
[7] Lin, J.T.; Sun, S.S.; Wu; J.J., Lee, L.; Lin, K.J.; Huang, Y.F., *Inorg. Chem.*, 1995, 34, 2323.
[8] Tang, L.; Yang, P., *Trans. Met. Chem.*, 2004, 29, 31.
[9] Gutman, T.; Dombrowski, E.; Burzlaff, N.; Schenk, W.A., *J. Organomet. Chem.*, 1998, 552, 91.
[10] Peters, R.G.; Bennet, B.L.; Schanbel, R.C.; Rodick, D.M., *Inorg. Chem.*, 1997, 36, 5926.
[11] Schenk, W.A.; Gutman, T., *J. Organomet. Chem.*, 1997, 544, 69.
[12] Mague, J.T., *J. Coord. Chem.*, 1997, 41, 327.
[13] El-khateeb, M.; Asali, K.J.; Musa, M.M., *Trans. Met. Chem.*, 2002, 27, 163.
[14] Asali, K.J.; El-khateeb, M.; Musa, M.M., *J. Coord. Chem.*, 2002, 55,1199.
[15] Asali, K.J.; Ladogana, T.; Bott, S.G.; Dobson, G.R., *J. Chem. Crystal.* 2003**,** 33, 701.
[16] Asali, K.J.; El-khateeb, M.; Battaineh, T.T., *Synth. Reac. Inorg. Met.-Org. Chem.*, 2003, 33, 1047.
[17] Asali, K.J.; El-khateeb, M.; Salhab, R., *Trans. Met. Chem.*, 2003**,** 28, 544.
[18] Asali, K.J.; El-khateeb, M.; Al-Hmaideen, A., *Jord. J. Chem.*, 2006, 1, 73.
[19] Dobson, G.R.; Taylor, R.C.; Walsh, T.D., *Inorg. Chem.*, 1967**,** 6, 1929.
[20] Asali, K.J.; Gideon, V.Z.; Dobson, G.R., *Inorg. Chem.*, 1998, 27, 3314.
[21] Dobson, G.R.; Houk, L.W., *Inorg. Chim. Acta* 1967, 1, 287.
[22] Chatt, J.; Watson, H.R., *J. Chem. Soc.*, 1961, 4980.
[23] Chatt, J., Hart, F.A., *J. Chem. Soc.*, 1960, 1378.

[24] a) Darensbourg, D.J.; Zalewski, D.J.; Plepys, C.; Campana, C., *Inorg. Chem.*, 1987, 26, 3727; b) Yang, C.C; Yeh, W.Y.; Lee, G.H.; Peng, S.M., *J. Organomet. Chem.*, 2000, 598, 353.
[25] Garrou, P.E., *Chem. Rev.*, 1981, 81, 229, and references therein.
[26] Gan, K.G.; Lee, H.K.; Hor, T.S.A., *J. Organomet. Chem.*, 1993, 460, 197.
[27] Grim, S.O.; Wheathland, D.A.; McAllister, P.M., *Inorg. Chem.*, 1968, 7, 161.
[28] Kieter, R.L., *J. Am. Chem. Soc*, 1995, 117, 7297.
[29] Ueng, C.H; Hwang, J.L., *Inorg. Chim. Acta*, 1994, 128, L3.
[30] Fujita, M.; Tominaga, M.; Hori, A.; Therrien, B., *Acc. Chem. Res.,* 2005, 38, 371, and references therein.
[31] Darensbourg, D.J., *Adv. Organomet. Chem.*, 1982, 21, 113.
[32] Howell, J.A.S.; Burkinshaw, P.M., *Chem. Rev.*, 1983, 83, 557, and references therein.
[33] Reinus, H.K.; Laitinen, R.H.; Karause, A.O.I.; Pursianen, J., *Catal. Lett.*, 1999, 60, 65.
[34] Tang, L.F.; Wang, Z.H.; Chai, J.F.; Leng, X.B.; Wang, J.T.; Wang, H.G., *J. Organomet. Chem.*, 2002, 642, 179.
[35] Brown, T.L.; Lee, K.J., *Coord. Chem. Rev.*, 1993, 128, 1993.
[36] Berstrom, C.L.; Luck, R.T., *Inorg. Chim. Acta*, 2001, 318, 77.
[37] Dyson, P.J., *Coord. Chem. Rev.*, 2004, 248, 2443.