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The Reactions of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo and W).
Part 2. New Synthesis of $[MI_2(CO)_3L_2]$ ($L = PPh_3$, $AsPh_3$ and $SbPh_3$) and the Rearrangement of the Bisphosphine Complexes to $[PPh_3H][MI_3(CO)_3(PPh_3)]$

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There is considerable interest in complexes of the type $[MX_2(CO)_3L_2]$ (M = Mo or W, $L = PPh_3$ or $AsPh_3$, X = Cl or Br) which are currently under investigation as catalysts for the ring opening polymerisation of norbornene [1, 2]. It is highly likely that the iodide complexes could also be useful as catalysts, but it has been difficult to prepare these complexes in the past. For example reaction of $[Mo(\mu\text{-}I)I(CO)_4]_2$ with PPh_3 affords the salt $[PPh_3H][MoI_3(CO)_3(PPh_3)]$ [3], and reaction of $[Mo(CO)_3(PPh_3)_3]$ with I_2 also gives the unusual anionic molybdenum compound $[PPh_3H][MoI_3(CO)_3(PPh_3)]$ [4]. We now report a new synthetic route to the complexes $[MI_2(CO)_3L_2]$ (M = Mo and W, $L = PPh_3$, $AsPh_3$ and $SbPh_3$), and investigate the subsequent rearrangement of the bisphosphine complexes to the anionic compounds $[PPh_3H][MI_3(CO)_3(PPh_3)]$.

Experimental

$[MI_2(CO)_3(NCMe)_2]$ were prepared according to literature methods [5], and PPh_3, $AsPh_3$ and $SbPh_3$ were purchased from Aldrich Chemical Company.

Infrared spectra were recorded on a Perkin-Elmer 197 infrared spectrophotometer. The elemental analyses for carbon, hydrogen and nitrogen were recorded on a Carlo Erba Elemental Analyser MOD1106 (using a helium carrier gas).

$MoI_2(CO)_3(PPh_3)_2$ (1)

$MoI_2(CO)_3(NCMe)_2$ (0.24 g, 0.465 mmol) was dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry argon. To this was added PPh_3 (0.244 g, 0.930 mmol). The colour of the solution immediately changed to a green–yellow. The mixture was left stirring for 1 min. Removal of the solvent *in vacuo* afforded the analytically pure green crystalline complex $[MoI_2(CO)_3(PPh_3)_2]$ (yield = 0.36 g, 81%).

$WI_2(CO)_3(PPh_3)_2$ (2)

$WI_2(CO)_3(NCMe)_2$ (0.42 g, 0.696 mmol) was dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry argon. To this was added PPh_3 (0.365 g, 1.392 mmol). The colour of the solution immediately changed to a pale yellow. The mixture was left stirring for 1 min. Removal of the solvent *in vacuo* afforded the analytically pure yellow complex $[WI_2(CO)_3(PPh_3)_2]$ (yield = 0.654 g, 89%).

$[PPh_3H][MoI_3(CO)_3(PPh_3)]$ (3)

$MoI_2(CO)_3(PPh_3)_2$ (0.199 g, 0.208 mmol) was dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry argon. The mixture was left stirring for 4 h after which time a yellow precipitate of $[PPh_3H][MoI_3(CO)_3(PPh_3)]$ was observed in the solution. This was filtered and dried under vacuum (yield = 0.08 g, 35%).

$[PPh_3H][WI_3(CO)_3(PPh_3)]$ (4)

$WI_2(CO)_3(PPh_3)_2$ (0.20 g, 0.191 mmol) was dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry argon. The mixture was left stirring for 19 h after which time a yellow–green precipitate of $[PPh_3H][WI_3(CO)_3(PPh_3)]$ was observed in the solution. This was filtered and dried under vacuum (yield = 0.06 g, 27%).

$MoI_2(CO)_3(AsPh_3)_2$ (5)

$MoI_2(CO)_3(NCMe)_2$ (0.45 g, 0.872 mmol) was dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry argon. To this was added $AsPh_3$ (0.534 g, 1.744 mmol). The colour of the solution immediately changed to a dark orange. The mixture was left stirring for 11 min. Removal of the solvent *in vacuo* afforded the analytically pure yellow crystalline complex $[MoI_2(CO)_3(AsPh_3)_2]$ (yield = 0.695 g, 76%).

$WI_2(CO)_3(AsPh_3)_2$ (6)

$WI_2(CO)_3(NCMe)_2$ (0.43 g, 0.712 mmol) was dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry argon. To this was added $AsPh_3$ (0.436 g, 1.424 mmol). The colour of the solution immediately changed to a dark yellow. The mixture was left stirring for 4 min. Removal of the solvent *in vacuo* afforded the analytically pure yellow–green complex $[WI_2(CO)_3(AsPh_3)_2]$ (yield = 0.76 g, 94%).

$MoI_2(CO)_3(SbPh_3)_2$ (7)

$MoI_2(CO)_3(NCMe)_2$ (0.45 g, 0.872 mmol) was dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry argon. To this was added $SbPh_3$ (0.616 g, 1.745 mmol). The colour of the solution changed to a dark orange. The mixture was

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TABLE I. Analytical (C, H and N)[a] and IR Data[b] for $[MI_2(CO)_3L_2]$ and $[PPh_3H][MI_3(CO)_3(PPh_3)]$

Complex	Analysis (%)[a]	ν(CO)[b] (cm^{-1})	ν(P–H)[b] (cm^{-1})
$[MoI_2(CO)_3(PPh_3)_2]$ (1)	C, 48.78(48.88) H, 3.40(3.12)	2020(m), 1962(s) and 1926(s)	
$[WI_2(CO)_3(PPh_3)_2]$ (2)	C, 44.92(44.74) H, 3.00(2.89)	2000(s), 1935(s) and 1918(s)	
$[PPh_3H][MoI_3(CO)_3(PPh_3)]$ (3)	C, 43.06(43.12) H, 3.16(2.88)	2010(m), 1938(s) and 1910(m)	2370(w)
$[PPh_3H][WI_3(CO)_3(PPh_3)]$ (4)	C, 40.18(39.89) H, 2.76(2.66)	2005(s), 1928(s) and 1905(s)	2380(w)
$[MoI_2(CO)_3(AsPh_3)_2]$ (5)	C, 44.82(44.77) H, 3.00(2.89)	2015(s), 1950(s) and 1910(s)	
$[WI_2(CO)_3(AsPh_3)_2]$ (6)	C, 41.03(41.30) H, 2.78(2.67)	2010(s), 1940(s) and 1904(s)	
$[MoI_2(CO)_3(SbPh_3)_2]$ (7)	C, 40.90(41.09) H, 2.75(2.65)	2020(s), 1959(s) and 1915(m)	
$[WI_2(CO)_3(SbPh_3)_2]$ (8)	C, 37.96(38.15) H, 2.58(2.46)	2015(s), 1945(s) and 1910(m)	

[a] Calculated values in parenthesis. [b] Spectra recorded in $CHCl_3$ unless stated: w, weak; m, medium; s, strong.

left stirring for 10 min. Removal of the solvent *in vacuo* afforded the analytically pure orange–brown crystalline complex $[MoI_2(CO)_3(SbPh_3)_2]$ (yield = 0.85 g, 86%).

$WI_2(CO)_3(SbPh_3)_2$ (8)

$WI_2(CO)_3(NCMe)_2$ (0.45 g, 0.745 mmol) was dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry argon. To this was added $SbPh_3$ (0.526 g, 1.490 mmol). The colour of the solution changed to a dark orange–yellow. The mixture was left stirring for 9 min. Removal of the solvent *in vacuo* afforded the analytically pure orange complex $[WI_2(CO)_3(SbPh_3)_2]$ (yield = 0.80 g, 83%).

Results and Discussion

Microanalytical data (C, H and N) and infrared spectroscopy (Table I) support the formulation of the complexes $[MI_2(CO)_3L_2]$ (M = Mo and W; L = PPh_3, $AsPh_3$ and $SbPh_3$) and $[PPh_3H][MI_3(CO)_3(PPh_3)]$ (M = Mo and W).

Under mild conditions two acetonitrile ligands are readily replaced from $[MI_2(CO)_3(NCMe)_2]$ by two PPh_3, $AsPh_3$ or $SbPh_3$ ligands. Since the complexes $[MI_2(CO)_3(NCMe)_2]$ can be prepared in high yield, and the reaction of the compounds with two equivalents of PPh_3, $AsPh_3$ or $SbPh_3$ also give near-quantitative yields, this has proved an excellent method for the synthesis of these important compounds. The two previously reported methods involved either reaction of the ligands with the iodide bridged dimer $[M(\mu\text{-}I)I(CO)_4]_2$ (which can only be made in poor yield) [3] or reaction of the complexes $[M(CO)_3L_3]$ (which are difficult to synthesise in high yield) [4] with iodine are not as efficient as the new method we are reporting in this communication.

It is also interesting to note that the bisphosphine complexes $[MI_2(CO)_3(PPh_3)_2]$ react in CH_2Cl_2 or $CHCl_3$ to give the well-known anionic complexes $[PPh_3H][MI_3(CO)_3(PPh_3)]$ probably via a disproportionation reaction. In the case of tungsten we have evidence to suggest that another product of this reaction is the metal–metal bonded dimer $[W(\mu\text{-}I)(CO)_2(PPh_3)_2]_2$, and we are currently investigating the mechanism of this reaction.

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