

Preliminary communication

# Syntheses of polymethylene bridged early–late transition metal complexes

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## Abstract

Reaction of the iodoalkyl complexes  $[LM\{(CH_2)_nI\}]$  of tungsten, rhenium, iron or ruthenium with the square planar Pt(II) complexes  $[PtMe_2(N-N)]$  leads to the formation of polymethylene-bridged heterobimetallic complexes of the general formula  $[LM(CH_2)_nPtIME_2(N-N)]$  in high yields. © 1998 Elsevier Science S.A. All rights reserved.

*Keywords:* Heterobimetallics; Oxidative addition; Polymethylene bridge; Platinum; Tungsten; Iodoalkyl

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## 1. Introduction

Transition metal complexes incorporating hydrocarbon bridges between metal atoms are of great interest as they play a pivotal role in the development of binuclear and polynuclear organometallic chemistry [1]. Early and late transition metals linked with hydrocarbons could have novel properties and might lead to new applications [2]. The earlier synthesis of polymethylene bridged binuclear complexes of general formula  $[LM(CH_2)_nML]$  (where ML is the metal and associated ligands) was limited to the reaction of transition metal anions  $[ML]^-$  with 1,*n*-dihaloalkanes [3]. The ability to isolate monometalated intermediate complexes  $[LM\{(CH_2)_nX\}]$  (*X* = halogen) in these reactions allowed the synthesis of heterobimetallic complexes with saturated hydrocarbon bridges  $[L'M'(CH_2)_nML]$  [4–6], by the reaction of metal anions  $[M'L']^-$  with functionalized metal alkyl complexes  $[LM\{(CH_2)_nX\}]$  (where LM is the metal and associated ligands and *X* is a functional group, e.g. Cl, Br, I etc). This method,

however, can only be applied to metals where the anions can be generated conveniently, such as  $[CpM(CO)_2]^-$  (*M* = Fe, Ru),  $[CpM(CO)_3]^-$  (*M* = Mo, W), etc. On the other hand, oxidative addition of 1,*n*-dihaloalkanes to low oxidation state transition metal complexes has been reported for the preparation of polymethylene bridged homobinuclear complexes of Rh [7], Co [8] and Pt [9–11].

We now report the general synthesis of polymethylene-bridged heterobimetallic complexes  $[LM(CH_2)_nPtIME_2(N-N)]$ , by the oxidative addition of iodoalkyl complexes,  $[LM\{(CH_2)_nI\}]$  to square planar complexes  $[PtMe_2(N-N)]$  [*N-N* = 4,4'-dimethyl-2,2'-bipyridine (*Me*<sub>2</sub>-bipy), and 2,2'-bipyridine (bipy)]. This method is effective and versatile for a range of polymethylene bridged heterobimetallic complexes.

## 2. Results and discussion

The bromoalkyl complexes  $[(\eta^5-C_5R_5)W(CO)_3\{(CH_2)_nBr\}]$  (*R* = H, *n* = 3, **1** [12], *n* = 4, **2** [12], *n* = 5, **3**; *R* = CH<sub>3</sub>, *n* = 3, **4**, *n* = 4, **5**), prepared by the reactions of  $Na[(\eta^5-C_5R_5)W(CO)_3]$  with 1,*n*-dibromoal-

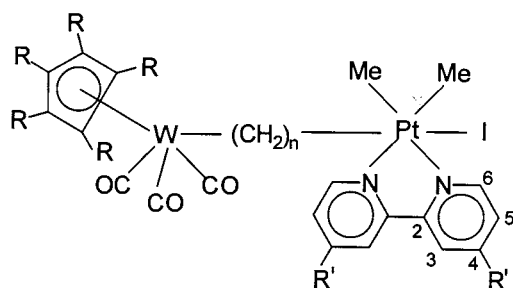
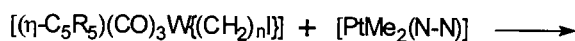
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kanes, were converted to their corresponding iodoalkyl analogous  $[(\eta^5\text{-C}_5\text{R}_5)\text{W}(\text{CO})_3\{(\text{CH}_2)_n\text{I}\}]$  ( $\text{R} = \text{H}$ ,  $n = 3$ , **6** [13],  $n = 4$ , **7,  $n = 5$ , **8**;  $\text{R} = \text{CH}_3$ ,  $n = 3$ , **9**,  $n = 4$ , **10**) in good yields (56–70%), by reacting them with NaI in acetone at room temperature for 1–2 days. The reaction of **1** with LiI was previously reported to give the *trans*-2-oxacyclopentylidene complex  $[\text{Cp}(\text{CO})_2\text{IW}(\text{COCH}_2\text{CH}_2\text{CH}_2)]$  [14].**

The square planar Pt(II) complexes  $[\text{PtMe}_2(\text{N-N})]$  ( $\text{N-N} = \text{bipy}$ , **11** [15],  $\text{Me}_2\text{-bipy}$ , **12** [16]) are electron rich, and among the most active of noble-metal complexes in oxidative addition reactions. Complex **12** was synthesized from  $[\text{Pt}_2\text{Me}_4(\text{SMe}_2)_2]$  [15] and  $\text{Me}_2\text{-bipy}$  and isolated as an orange solid in yields 71–88%.

The square planar Pt(II) complexes **11** or **12** reacted cleanly with the iodoalkyl complexes **6–10**, to produce  $[(\eta^5\text{-C}_5\text{R}_5)\text{W}(\text{CO})_3(\text{CH}_2)_n\text{Pt}(\text{N-N})\text{Me}_2]$ , (**13–22**, see Scheme 1), in dry acetone or benzene at room temperature. The yellow products (**13–22**) were obtained in



R	R'	n	Compound no.	Yield (%)
H	H	3	<b>13</b>	79
H	H	4	<b>14</b> [17]	92
H	H	5	<b>15</b>	74
H	CH <sub>3</sub>	3	<b>16</b>	69
H	CH <sub>3</sub>	4	<b>17</b>	52
H	CH <sub>3</sub>	5	<b>18</b>	78
CH <sub>3</sub>	H	3	<b>19</b>	72
CH <sub>3</sub>	H	4	<b>20</b>	85
CH <sub>3</sub>	CH <sub>3</sub>	3	<b>21</b>	82
CH <sub>3</sub>	CH <sub>3</sub>	4	<b>22</b>	83

Scheme 1. Schematic presentation and numbering of the heterobimetallic compounds (**13–22**).

high yields after recrystallization from  $\text{CH}_2\text{Cl}_2/\text{hexane}$ . The products of these reactions are a result of *trans*-addition of the iodoalkyl complexes, to the square planar Pt(II) centre and have been characterized by their  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra as well as elemental analyses and IR spectra.

Thus, the IR spectrum of the new complex **17** shows two strong bands at 2009 and 1909  $\text{cm}^{-1}$  in the carbonyl region in  $\text{CH}_2\text{Cl}_2$ , which is similar to that of the starting iodoalkyl complex **2**. The UV-visible spectrum of the starting complex **12** shows the presence of a platinum(II) *5d*-diimine ( $\pi^*$ ) metal-to-ligand charge transfer (MLCT) band at  $\lambda_{\text{max}} = 464$  nm. For the product **17**, a band at  $\lambda_{\text{max}} = 362$  nm is observed, which is in agreement with the change from Pt(II) to Pt(IV).

The characteristic peaks of the iodoalkyl complex **6** at  $\delta$  3.11 ppm due to  $\text{CH}_2\text{I}$  in the  $^1\text{H}$ -NMR spectrum disappeared after reaction, in agreement with the oxidative addition reaction having taken place at this site. The protons of the methylene group now directly bonded to platinum in **13** appear as a triplet with  $^{195}\text{Pt}$  satellites at 1.34 ppm with  $^2J_{\text{PtH}}$  equal to 70 Hz. Only one sharp PtMe resonance is observed at 1.50 ppm with  $^2J_{\text{PtH}}$  equal to 71 Hz. This is good evidence that the complex **13** retains the methyl groups *trans* to the bipyridine ligand. The resonance due to the  $\text{WCH}_2$  protons is observed as a distorted triplet at 1.17 ppm, no  $^{183}\text{W}$ -H coupling is observed. The proton resonance of the Cp ligand appears as a single peak at 5.15 ppm. The other protons of the bipyridine ligand are observed at 7.65, 8.09, 8.20 and 9.00 ppm.

The  $^{13}\text{C}$ -NMR spectrum of complex **14** [17] shows the resonances associated with the polymethylene chain  $\text{WCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Pt}$  at  $-10.42$ ,  $36.37$  ( $^3J_{\text{Pt-C}}$  29 Hz),  $37.95$  ( $^2J_{\text{Pt-C}}$  87 Hz) and  $26.51$  ( $^1J_{\text{Pt-C}}$  661 Hz) ppm in  $\text{CDCl}_3$ . The Pt-C coupling constants ( $^nJ_{\text{Pt-C}}$ ) were useful for the assignments of the  $^{13}\text{C}$  signals. No  $^4J_{\text{Pt-C}}$  coupling is observed. The resonance of PtMe gave only one signal at  $-4.65$  ppm with  $^1J_{\text{Pt-C}}$  693 Hz, which is in agreement with the *trans*-oxidative addition.

In the electrospray (ES) mass spectrum of **22** ( $M_w$  995.50) in  $\text{CH}_3\text{CN}$ , at high cone voltage (50 V), high mass peaks in the range  $m/z$  865–873 were observed, which correspond to  $[\text{M-I}]^+$ , with expected platinum and tungsten isotope patterns. At low cone voltage (15 V), peaks due to  $[\text{M-I} + \text{CH}_3\text{CN}]^+$  were found. FAB mass spectra of the heterobimetallic complexes **13**, **14**, and **17** also show peaks corresponding to  $[\text{M-I}]^+$ . A conductivity measurement of the complex **21** in nitrobenzene confirmed that it is a non-electrolyte.

We also find that the oxidative addition reactions of iodoalkyl complexes to Pt(II) complexes are quite general. Thus, reactions of  $[(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2\{(\text{CH}_2)_n\text{I}\}]$  [5,6] ( $n = 4$ ,  $\text{R} = \text{H}$ , **22**,  $\text{CH}_3$ , **23** [18]),  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2\{(\text{CH}_2)_n\text{I}\}]$  [6] ( $n = 4$ , **24**) and  $[\text{Re}(\text{CO})_5\{(\text{CH}_2)_n\text{I}\}]$  [19] ( $n = 4$ , **25**) with **12** gave  $[(\eta^5\text{-C}_5\text{R}_5)\text{W}(\text{CO})_3(\text{CH}_2)_n\text{Pt}(\text{N-N})\text{Me}_2]$  (**13–22**).

$C_5R_5Fe(CO)_2(CH_2)_nPtIme_2(N-N)$  ( $N-N = Me_2$ -bipy,  $n = 4$ ,  $R = H$ , **26**,  $R = CH_3$ , **27**),  $[(\eta^5-C_5H_5)Ru(CO)_2-(CH_2)_nPtIme_2(N-N)]$  ( $N-N = Me_2$ -bipy,  $n = 4$ , **28**) and  $[Re(CO)_5(CH_2)_nPtIme_2(N-N)]$  ( $N-N = Me_2$ -bipy,  $n = 4$ , **29**), in 67, 98, 63 and 78% yields, respectively. These complexes have been fully characterized by spectroscopic methods which show the products to be the result of *trans*-oxidative addition.

In conclusion, simple procedures have been developed which make iodoalkyl complexes readily available precursors for the synthesis of a range of new polymethylene bridged heterobinuclear complexes. The chemistry of these complexes and their potential applications will be the subject of future papers.

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- [17] **14** (containing one mole solvent  $CH_2Cl_2$  per mole **14**) mp. 185–190 °C dec. IR ( $CH_2Cl_2$ ):  $\nu(CO)$  2009s, 1909s ( $cm^{-1}$ ). UV-visible: (acetone)  $\lambda_{max} = 362$  nm.  $^1H$ -NMR ( $CDCl_3$ ):  $\delta$  8.98 (2H, m), 8.21 (2H, d,  $J$  8 Hz), 8.07 (2H, m), 7.63 (2H, m), 5.30 (2H, s,  $CH_2Cl_2$ ), 5.27 (5H, s, Cp), 1.50 (6H, s,  $^2J_{PtH}$  71 Hz), 1.38 (2H, distorted tri,  $^2J_{PtH}$  ca. 70 Hz), 1.28–1.17 4H, m,  $WCH_2$  and  $WCH_2CH_2$ ), 0.44 (2H, m, Pt $CH_2$ ).  $^{13}C$ -NMR ( $CDCl_3$ ):  $\delta$  228.77 (CO), 217.46 (CO), 154.91 (ring  $C_2$ ), 147.47 (ring  $C_6$ ), 138.59 (ring  $C_4$ ), 126.73 (ring  $C_5$ ), 123.36 (ring  $C_3$ ), 91.41 (Cp), 53.41 ( $CH_2Cl_2$ ), 37.95 ( $^2J_{PtC}$  87 Hz, Pt $CH_2CH_2$ ), 36.47 ( $^3J_{PtC}$  29 Hz,  $WCH_2CH_2$ ), 26.51 ( $^1J_{PtC}$  662 Hz, Pt $CH_2$ ), –4.65 ( $^1J_{PtC}$  693 Hz, PtMe), –10.42 ( $WCH_2$ ). FAB MS:  $m/z$  768  $[M-I]^+$ .
- [18] **23** mp. 203–205°C dec. IR ( $CH_2Cl_2$ ):  $\nu(CO)$  1978s, 1914s ( $cm^{-1}$ ). UV-visible: (acetone)  $\lambda_{max} = 354$  nm.  $^1H$ -NMR ( $CDCl_3$ ):  $\delta$  8.78 (2H, m,  $H_6$ ), 8.01 (2H, s, H), 7.39 (2H, d,  $J$  4.8 Hz,  $H_5$ ), 2.53 (6H, s, ring Me), 1.62 (15H, s,  $C_5(CH_3)_5$ ), 1.45 (6H, s,  $^2J_{PtH}$  72 Hz, PtMe), 1.39 (2H, m,  $^2J_{PtH}$  72 Hz, Pt $CH_2$ ), 1.10 (2H, qn,  $J$  8 Hz,  $CH_2CH_2$ ), 0.60 (2H, distorted tri,  $J$  7.6 Hz,  $WCH_2$ ), 0.50 (2H, M, Pt $CH_2CH_2$ ).  $^{13}C$ -NMR ( $CDCl_3$ ):  $\delta$  219.50 (CO), 154.82 (ring  $C_2$ ), 150.27 (ring  $C_4$ ), 146.79 (ring  $C_6$ ), 127.40 (ring  $C_5$ ), 123.97 (ring  $C_3$ ), 94.70 ( $C_5(CH_3)_5$ ), 38.66 ( $^2J_{PtC}$  81 Hz, Pt $CH_2CH_2$ ), 36.31 ( $^3J_{PtC}$  29 Hz, Fe $CH_2CH_2$ ), 27.33 ( $^1J_{PtC}$  661 Hz, Pt $CH_2$ ), 21.59 (ring Me), 13.05 (Fe $CH_2$ ), 9.27 ( $C_5(CH_3)_5$ ), –4.97 ( $^1J_{PtC}$  697 Hz, PtMe).
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