## COMMUNICATION

## DIHAPTO-ACYL VERSUS ALKYL(CARBONYL) COORDINATION. INFLUENCE OF ELECTRONIC AND STERIC EFFECTS

## E. CARMONA\* and L. SÁNCHEZ

Departamento de Química Inorgánica, Facultad de Química, Universidad de Sevilla, e Instituto de Ciencias de Materiales de Sevilla, CSIC., Aptdo. 553, Sevilla, Spain

(Received 16 July 1987; accepted 8 September 1987)

Abstract—The synthesis and characterization of a series of seven-coordinate methyl-(carbonyl)- and the related six-coordinated  $\eta^2$ -acyl complexes of tungsten [e.g. W(CH<sub>3</sub>) Cl(CO)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub>, W( $\eta^2$ -COR)(S<sub>2</sub>CNMe<sub>2</sub>)(CO)(PMe<sub>3</sub>)<sub>2</sub>, etc.] were carried out to explore the influence of electronic and steric effects. By changing the nature of the R group and/or of the ancillary ligands, it is shown that a decrease in the electron density at the metal centre and an increase in the steric requirements of the R group, favour the  $\eta^2$ -acyl structure over the alkyl(carbonyl) formulation.

Recent work from several laboratories has allowed characterization of a growing number of formally six-coordinate  $\eta^2$ -acyl complexes of molybdenum<sup>1-3</sup> and tungsten,<sup>4-5</sup> e.g. Mo( $\eta^2$ -COR)X(CO) (PMe<sub>3</sub>)<sub>3</sub>,<sup>3</sup> TpMo( $\eta^2$ -COR)(CO)<sub>2</sub><sup>1b,2</sup> but the corresponding seven-coordinate alkyl(carbonyl) derivatives have not been found to occur. Since the interconversion of formulations **A** and **B** does not



\* Author to whom correspondence should be addressed.

<sup>†</sup>Compounds **1a–1d** were prepared by a route similar to that reported for the molybdenum analogs (ref. 3). Selected spectroscopic data for **1a** and **1b** are as follows: **1a**, IR (Nujol): νCO 1890, 1790 cm<sup>-1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.3 (broad, PMe<sub>3</sub>), 0.4 (pseudoquartet, W-CH<sub>3</sub>). <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  –27.2 (t, <sup>2</sup>J<sub>P<sub>A</sub>P<sub>X</sub></sub> = 28.6 Hz), -22.15(d). Although stable as a solid when kept under N<sub>2</sub>, **1a** decomposes in solution with the formation of WCl<sub>2</sub>(CO)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> and other unidentified species. **1b**, IR(KBr): νCO 1800 cm<sup>-1</sup>, νCOR 1460 cm<sup>-1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  2.9 (s, CH<sub>2</sub>SiMe<sub>3</sub>), 1.34 (d, <sup>2</sup>J<sub>HPA</sub> = 7.8 Hz, P<sub>A</sub>Me<sub>3</sub>), 1.15 (t, <sup>2</sup>J<sub>ap(HPB)</sub> = 3.1 Hz, P<sub>B</sub>Me<sub>3</sub>), 0.17 (s, CH<sub>2</sub>SiMe<sub>3</sub>); <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>): AB<sub>2</sub> system,  $\delta_A = -14.4, \delta_B = -14.8$  ppm, <sup>2</sup>J<sub>P<sub>A</sub>P<sub>a</sub></sub> = 10.4 Hz. change the number of electrons at the metal centre, it was reasoned that in a series of analogous complexes, structure **B** should be favoured with respect to **A** for sterically demanding **R** groups, while an increase in the electron density at the metal centre, i.e. of the metal basicity, would favour formulation **A**, because of the strong acceptor properties of the carbonyl ligand. In this communication we present preliminary results which clearly show the influence of the steric and electronic effects on the relative stability of structures **A** and **B**, and report, for the first time, the controlled formation of both types of complexes and of an equilibrium mixture of the above structures.

The alkylation of complexes  $MCl_2(CO)_2$ (PMe<sub>3</sub>)<sub>3</sub><sup>6</sup> yields the  $\eta^2$ -acyls  $M(\eta^2$ -COR)Cl(CO) (PMe<sub>3</sub>)<sub>3</sub>, or the alkyl(carbonyl), W(Me)Cl(CO)<sub>2</sub> (PMe<sub>3</sub>)<sub>3</sub>, **1a**, as shown in eqs (1) and (2).

$$MCl_2(CO)_2(PMe_3)_3 + Mg(R)Cl$$

$$\rightarrow M(\eta^2 - COR)Cl(CO)(PMe_3)_3 + MgCl_2 \quad (1)$$

 $(M = Mo, ref. 3; M = W, R = CH_2SiMe_3, 1b; CH_2CMe_3, 1c; CH_2CMe_2Ph, 1d)$ 

 $WCl_2(CO)_2(PMe_3)_3 + LiMe$ 

 $\rightarrow$  W(Me)Cl(CO)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub>+LiCl. (2)

The new compounds have been fully characterized by analytical and spectroscopic studies,<sup>†</sup> which show the  $\eta^2$ -acyls have structures of type C,



similar to those found for the molybdenum analogs.<sup>3</sup> The structure of 1b (as well as that of 2a, see below) has been determined by X-ray crystallography and will be reported elsewhere. Complexes 1a-1d do not rearrange into their corresponding isomeric forms, i.e.  $A \rightleftharpoons B$ , upon thermal or photochemical activation. Since on the other hand no exchange between the CO groups of the acyl and carbonyl ligands is detected by <sup>13</sup>C NMR studies, these compounds are assumed to be the thermodynamic products of the above reactions. Therefore, the  $\eta^2$ -acyl structure is favoured for the above complexes with the only exception being the W-CH<sub>3</sub> derivative for which the alkyl-carbonyl formulation is preferred. We propose that this difference is due to a combination of electronic and steric effects. The former would make the alkyl(carbonyl) structure, A, more stable\* in the order Mo < W because of the higher basicity of the tungsten derivatives,<sup>8</sup> while the latter are obviously responsible for the stabilization of the  $\eta^2$ -acyl structure for the bulkier  $CH_2SiMe_3$ ,  $CH_2CMe_3$  and  $CH_2CMe_2Ph$  alkyl groups.<sup>†</sup>

The reaction of  $Mo(\eta^2$ -COR)Cl(CO)(PMe<sub>3</sub>)<sub>3</sub> complexes with the sodium salt of the strongly electron releasing Me<sub>2</sub>NCS<sub>2</sub><sup>-</sup> ligand proceeds with formation of the  $\eta^2$ -acyls  $Mo(\eta^2$ -COR)(S<sub>2</sub>CNMe<sub>2</sub>)

\* Both the strength of the M—C bond (5d > 4d) and the migratory aptitude of the alkyl group also favour structure **A** for the W—CH<sub>3</sub> complex.<sup>7</sup> However, a decrease in the electron density at the metal centre, caused by substitution of one PMe<sub>3</sub> ligand by CO (see Text), makes structure **B** the more favourable.

<sup>†</sup>A similar situation, although related to the steric effects of the ancillary ligands, has been found for the ruthenium complexes  $\text{Ru}(\eta^2\text{-}\text{COC}_6\text{H}_4\text{-}p\text{-}\text{CH}_3)X(\text{CO})$  (PPh<sub>3</sub>)<sub>2</sub>. For these compounds, <sup>9</sup> which exist in solution in equilibrium with the corresponding aryldicarbonyls, the tendency towards formation of the dihapto linkage increases in the order Cl < Br < 1.

<sup>‡</sup>Only the η<sup>2</sup>-acyl structure exists in the solid state : IR (Nujol) : νCO 1725 cm<sup>-1</sup>, νCOR is not observed, possibly due to overlapping with ν(C—N) of the S<sub>2</sub>CNR<sub>2</sub> ligand, 1490 cm<sup>-1</sup>. IR (C<sub>6</sub>D<sub>6</sub>): νCO 1900, 1810 and 1760 cm<sup>-1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): (a) W(R)(CO)<sub>2</sub>(S<sub>2</sub>CNMe<sub>2</sub>)(PMe<sub>3</sub>)<sub>2</sub>:  $\delta$  2.57 (s, S<sub>2</sub>CNMe<sub>2</sub>), 1.43 (d, PMe<sub>3</sub>), 0.14 (s, CH<sub>2</sub>SiMe<sub>3</sub>), -0.06 (t, <sup>3</sup>J<sub>HP</sub> = 5.4 Hz, W-CH<sub>2</sub>SiMe<sub>3</sub>). (b) W(COR) CO(S<sub>2</sub>CNMe<sub>2</sub>)(PMe<sub>3</sub>)<sub>2</sub>: 2.96 (s, COCH<sub>2</sub>SiMe<sub>3</sub>), 2.73 (s, S<sub>2</sub>CNMe<sub>2</sub>), 2.67 (s, S<sub>2</sub>CNMe<sub>2</sub>). 1.59 (t, PMe<sub>3</sub>), 0.47 (s, COCH<sub>2</sub>SiMe<sub>3</sub>).  $(\underline{CO})(\underline{PMe_3})_2$  and of the unusual acetyl  $\overline{Mo}(\underline{COCH_3})(\underline{S_2CNMe_2})(\underline{CO})(\underline{PMe_3})_2$ .<sup>3</sup> To determine the effect of this substitution reaction, which is accompanied by an increase in the electron density at the metal centre ( $\nu(\underline{C=O})$  decreases by *ca* 60 cm<sup>-1</sup>), in the relative stability of structures **A** and **B**, the reaction of complexes **1a–1d** with NaS<sub>2</sub>CNMe<sub>2</sub> has been investigated, <sup>10</sup> with the results shown in eqs (3) and (4).

$$W(CH_3)Cl(CO)_2P_3 + NaS_2CNMe_2$$

$$\rightarrow W(CH_3)(S_2CNMe_2)(CO)_2P_2 + NaCl \quad (3)$$

$$2a$$

$$W(\eta^2 - COR)Cl(CO)P_3 + NaS_2CNMe_2$$

$$\rightarrow W(\eta^2 - COR)(S_2CNMe_2)(CO)P_2 + P + NaCl$$

$$(4)$$

 $(\mathbf{R} = \mathbf{CH}_2\mathbf{SiMe}_3, \mathbf{2b}; \mathbf{CH}_2\mathbf{CMe}_3, \mathbf{2c}; \mathbf{CH}_2\mathbf{CMe}_2\mathbf{Ph}, \mathbf{2d}, \mathbf{P} = \mathbf{PMe}_3).$ 

Two aspects of this process deserve further comments. First, in light of the results reported in this paper, the unusual structure displayed by the molyb denum-acetyl complex<sup>3</sup> can be thought of as "mid-way" between the  $\eta^2$ -acyl and the methyl-(carbonyl) structures. This further supports our initial proposal<sup>3</sup> of structure **D** as a model for the



transition state (or intermediate) of the CO insertion into M—C bonds. (A similar structure has been proposed as a model for the formation of ketene and a metal hydride by  $\beta$ -elimination from a metal acetyl compound.)<sup>11</sup> The second point concerns the behaviour of complex **2b**, for which an equilibrium between the  $\eta^2$ -acyl and the alkyl-(carbonyl) formulation is quickly attained in solution [eq. (5)] as revealed by IR and NMR studies.<sup>‡</sup> Observation of

$$W(\eta^{2}\text{-}COCH_{2}SiMe_{3})(S_{2}CNMe_{2})$$

$$(CO)(PMe_{3})_{2} \xleftarrow{C_{6}H_{6}} W(CH_{2}SiMe_{3})$$

$$(S_{2}CNMe_{2})(CO)_{2}(PMe_{3})_{2} \quad (5)$$

both structures for **2b** and exclusively of the  $\eta^2$ -acyl isomer for **1b** is clearly electronic in origin and can be ascribed to the increase in the electron density at the metal centre which accompanies the transformation, of **1b** into **2b**. Note that the steric demands of the alkyl groups investigated in this work increase in the order CH<sub>3</sub> < CH<sub>2</sub>SiMe<sub>3</sub> < CH<sub>2</sub>CMe<sub>3</sub> < CH<sub>2</sub>CMe<sub>2</sub>Ph.

Confirmation of the above hypothesis, concerning the influence of electronic effects on the relative stability of structures A and B, requires that a sufficient decrease in the metal basicity causes transformation of the alkyl(carbonyl) species into the  $\eta^2$ -acyl. This decrease can be induced by substituting one of the strong  $\sigma$ -donor PMe<sub>3</sub> ligands<sup>12</sup> (cone angle<sup>13</sup>  $\theta = 118^{\circ}$ ), for the strongly  $\pi$ -acid and less steric demanding CO ligand ( $\theta = 95^{\circ}$ ). Indeed, the reaction of the methyl(carbonyl) complexes,  $W(CH_3)Cl(CO)_2(PMe_3)_3$  and  $W(CH_3)(S_2CNMe_2)$  $(CO)_2(PMe_3)_2$ , with carbon monoxide proceeds under mild conditions, with formation of the  $\eta^2$ -acetyls  $W(\eta^2$ -COCH<sub>3</sub>)Cl(CO)<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>, 3a and  $W(\eta^2$ -COCH<sub>3</sub>)(S<sub>2</sub>CNMe<sub>2</sub>)(CO)<sub>2</sub>(PMe<sub>3</sub>), 4a, respectively. Furthermore, action of CO upon an equilibrium mixture of  $W(\eta^2 - COCH_2SiMe_3)$  $(S_2CNMe_2)(CO)(PMe_3)_2$ and  $W(CH_2SiMe_3)$  $(S_2CNMe_2)(CO)_2(PMe_3)_2$ , produces only the  $\eta^2$ -acyl complex W( $\eta^2$ -COCH<sub>2</sub>SiMe<sub>3</sub>)(S<sub>2</sub>CNMe<sub>2</sub>)  $(CO)_2(PMe_3)$ , 4b. In the absence of steric constraints which could favour rearrangement of the alkyl(carbonyl) into the  $\eta^2$ -acyl, the transformation observed must be entirely ascribed to electronic factors.

The results described in this paper indicate that : (i) the relative stability of seven-coordinated alkyl-(carbonyl) complexes and their six-coordinated  $\eta^2$ acyl isomers is greatly influenced by steric and electronic effects; (ii) an increase in the metal basicity preferentially stabilizes the alkyl(carbonyl) isomer, while a decrease in the electron density at the metal centre favours formation of the  $\eta^2$ -acyl linkage;<sup>14</sup> (iii) as it could reasonably be expected, an increase in the steric demands of the alkyl group favours the  $\eta^2$ -acyl structure, while the less steric demanding alkyl groups prefer the alkyl(carbonyl) formulation.

Acknowledgements—Useful discussions with Dr M. L. Poveda and the generous support of this work by the

Comisión Asesora de Investigación Científica y Técnica (CAICYT) are very gratefully acknowledged.

## REFERENCES

- (a) E. Carmona, G. Wilkinson, R. D. Rogers, W. D. Hunter, M. J. Zaworotko and J. L. Atwood, J. Chem. Soc., Dalton Trans. 1980, 229; (b) T. Desmond, F. J. Lalor, G. Ferguson, B. Ruhl and M. Parvez, J. Chem. Soc., Chem. Commun. 1983, 55.
- (a) C. A. Rusik, T. L. Tonker and J. L. Templeton, J. Am. Chem. Soc. 1986, 108, 4652; (b) M. D. Curtis, K. B. Shiu and W. B. Butler, J. Am. Chem. Soc. 1986, 108, 1550.
- E. Carmona, L. Sánchez, J. M. Marín, M. L. Poveda, J. L. Atwood, R. D. Priester and R. D. Rogers, J. Am. Chem. Soc. 1984, 106, 3214.
- (a) E. Carmona, J. M. Marín, M. L. Poveda, L. Sánchez, R. D. Rogers and J. L. Atwood, J. Chem. Soc., Dalton Trans. 1983, 1003; (b) H. G. Alt, J. Organomet. Chem. 1977, 129, 349.
- 5. F. R. Kreissl, W. J. Sieber, M. Wolfgruber and J. Riede, Angew. Chem. Int. Ed. Engl. 1984, 23, 640.
- E. Carmona, K. Doppert, J. M. Marín, M. L. Poveda, L. Sánchez and R. Sánchez-Delgado, *Inorg. Chem.* 1984, 23, 530.
- H. Berke and R. Hoffmann, J. Am. Chem. Soc. 1978, 100, 7224.
- 8. D. F. Shriver, Acc. Chem. Res. 1970, 231.
- 9. W. R. Roper and L. J. Wright, J. Organomet. Chem. 1977, 142, C1.
- (The molecular structures of complexes 1b and 2a have been determined by X-ray crystallography.) R.
   D. Rogers and J. L. Atwood (to be submitted).
- 11. S. I. Hommeltoft and M. C. Baird, Organometallics 1986, 5, 190.
- M. N. Golovin, M. M. Rahman, J. E. Belmonte and W. P. Giering, Organometallics 1985, 4, 1981.
- 13. C. A. Tolman, Chem. Rev. 1977, 77, 313.
- J. L. Templeton, P. B. Winston and B. C. Ward, J. Am. Chem. Soc. 1981, 103, 7713.