Thermochimica Acta, 128 (1988) 175–184
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL DEGRADATION OF TRANSITION METAL CARBONYL COMPLEXES. PART III. THERMOGRAVIMETRIC AND DIFFERENTIAL SCANNING CALORIMETRIC STUDIES OF TRIPHENYLPHOSPHINE PENTACARBONYLS OF CHROMIUM, MOLYBDENUM AND TUNGSTEN

T.S. ANDY HOR *, HARDY S.O. CHAN, CAROLINE S.M. CHIAM
and KOK HWA LIM

Department of Chemistry, Faculty of Science, National University of Singapore, Kent Ridge, 0511 (Singapore)

(Received 31 August 1987)

ABSTRACT

Thermogravimetric and differential scanning calorimetric studies on $M(CO)_5(PPh_3)$ (M = Cr, Mo, W) revealed a sequential decomposition process which commenced at ca. 150 °C. The Cr complex breaks down with a concurrent liberation of one PPh_3 and two CO ligands. The Mo complex, however, eliminates two CO ligands stepwise, followed by the cleavage of the Mo–PPh_3 bond. Expulsion of the PPh_3 ligand in the W complex is facile, and occurs prior to the simultaneous elimination of the five CO ligands. Complete elimination of the ligands occurs readily in the latter complex below ca. 350 °C, which is consistent with a recent microcalorimetric study in the literature. The degradation pattern is dependent on the electronic and steric factors of the metal and ligands.

INTRODUCTION

Thermochemistry of organometallic reactions has been an area of intense research activity [1–3]. A thorough understanding of the enthalpy changes in different types of reaction, such as ligand dissociation and exchange, and isomerisation processes, is of fundamental importance in studying organometallic chemistry [4–6]. Thermochemical data thus obtained have been invaluable in the understanding of some subjects amongst which catalysis, kinetics and reaction mechanism are most important [7,8]. Unfortunately, studies of this nature have been complicated by the solvent-dependent properties of many reactions and the extreme air-sensitive nature of many interesting organometallic molecules. So far, most of the investigations have been confined to solution chemistry and flash photolysis in the gas phase [9–13].

---

* Author to whom correspondence should be addressed.

0040-6031/88/$03.50 © 1988 Elsevier Science Publishers B.V.

Thermogravimetry (TG) and differential scanning calorimetry (DSC) are among the well-established techniques in studying the thermal behaviour of many organic compounds and some Werner-type compounds [14–18]. We have recently initiated a programme for studying a fundamental class of metal carbonyls using these two thermal techniques [19]. Using triphenylphosphine-substituted Group 6 metal carbonyls as models, this paper aims to substantiate the understanding of metal–ligand bond cleavages.

EXPERIMENTAL

General procedure

All preparations were carried out under dry nitrogen. A standard procedure is described below. The purity of each complex was established by microanalyses and spectroscopic (IR [20], ^{1}H- and ^{31}P-NMR [21]) measurements and melting points, which were in agreement with literature values. Proton NMR spectra were recorded either on a JOEL FX 90Q or a Perkin–Elmer R32 NMR spectrometer at 90 MHz. ^{31}P-NMR spectra were recorded on the latter instrument at 36.23 MHz. IR spectra were run on a Unicam SP1000 spectrophotometer (in solution). Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry, National University of Singapore using a Perkin–Elmer elemental analyser. Melting points were determined by a Thomas Hoover capillary melting point apparatus and were uncalibrated.

Thermal analysis

All TG experiments were conducted on a Du Pont 9900 thermal analyser in dry nitrogen. The nitrogen flow was 75 cm^3 min^{-1} and the heating rate was 10 °C min^{-1}. The experiments were conducted from room temperature to 1000 °C. DSC experiments were carried out on the same instrument, calibrated to have a cell constant of 1.19. Nitrogen flow was 50 cm^3 min^{-1} and the temperature range was from room temperature to 600 °C. The same heating rate was applied. The enthalpy values were generated by computer, with indium as the reference.

Materials

Solvents used were of reagent grade and degassed before use. $M(CO)_6$ (M = Cr, Mo, W) and triphenylphosphine were purchased from Alfa Product Co. and Merck Schuchardt Chemical Co., respectively. Trimethylamine-*N*-oxide dihydrate (TMNO) was supplied by Aldrich Chemical Co. and Tokyo Kasei Kogyo Co. They were used without further purification.

Preparations

The syntheses of the complexes $M(CO)_5(PPh_3)(M = Cr, Mo, W)$ have been reported in the literature [20,21], but the method was modified in the present work. The use of TMNO in such syntheses enhances selectivity and hence simplifies isolating procedures [22]. A typical preparation is described below.

$Cr(CO)_5(PPh_3)$

$Cr(CO)_6$ (0.5017 g, 2.28 mmol) and TMNO (0.2540 g, 2.29 mmol) were added to acetonitrile (30 ml) to give a clear yellow solution. Triphenylphosphine (0.5979 g, 2.28 mmol) was added to the mixture, followed by stirring at room temperature for 16 h. The solution was filtered and the filtrate was cooled at −20 °C to yield pale yellow crystals. Recrystallizations were carried out in chloroform/ethanol. Yield = 0.61 g (59%), melting point = 127–129 °C (literature, melting point = 127–128 °C [23]). ν(CO): 2080m, 1990w, 1945vs, 1916m(sh). Analysis: found : C, 60.54%; H, 3.10%. $C_{23}H_{15}CrO_5P$: calc., C, 60.80%; H, 3.32%.

Preparations of $Mo(CO)_5(PPh_3)$ and $W(CO)_5(PPh_3)$ followed similar procedures. $Mo(CO)_5(PPh_3)$: m.p. = 138–139 °C (lit. 131–133 °C [23]). ν(CO) = 2080w, 1990vw, 1950vs. Analysis: found: C, 55.29%; H, 2.73%. $C_{23}H_{15}MoO_5P$: calc.: C, 55.44%; H, 3.03%. $W(CO)_5(PPh_3)$: m.p. = 143–144 °C (lit. 146–147 °C [23]). ν(CO) = 2080w, 1990vw, 1940vs, 1890w(sh). Analysis: found: C, 47.23%; H, 2.50%. $C_{23}H_{15}WO_5P$ calc.: C, 47.13%; H, 2.58%.

RESULTS: TG AND DSC ANALYSIS

$Cr(CO)_5(PPh_3)$

Thermogravimetric analysis

A large weight loss is observed over the temperature range 160–280 °C (Fig. 1). This huge weight loss can be attributed to the overlapping decomposition reactions and is confirmed by the presence of a number of peaks in the derivative thermogravimetric curve over that temperature range. The weight loss corresponds to the loss of one mole of PPh_3 and two moles of CO (obs., 68.9%; calc., 69.9%). The precise sequence of the elimination of the ligands is, however, uncertain. A smaller weight loss is registered at ca. 280–420 °C which can be explained by the elimination of another CO (obs., 5.4%; calc., 6.1%). The percentage weight of the residue corresponds to $Cr(CO)_2$ (obs., 25.5%; calc., 23.7%).

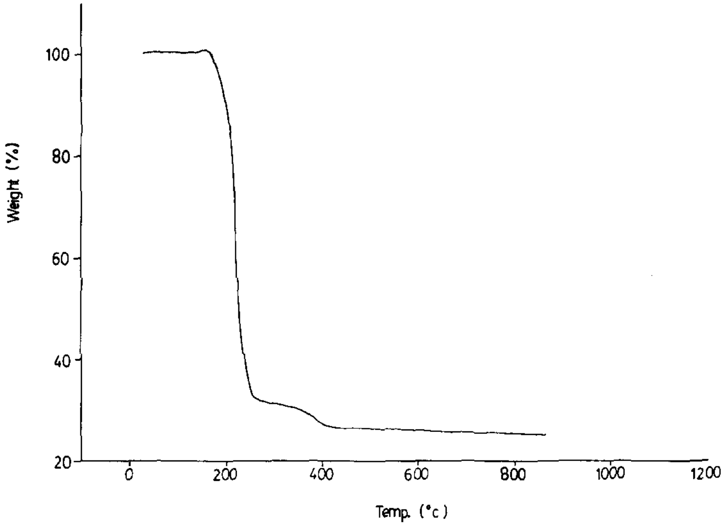

Fig. 1. TG curve of $Cr(CO)_5(PPh_3)$.

Differential scanning calorimetry

A sharp endothermic peak at 124 °C (Fig. 2) is consistent with the melting of the complex ($\Delta H = 29.7$ kJ mol^{-1}). A broad endothermic peak starting at ca. 230 °C is due to the overlapping reactions involving the expulsion of two moles of CO and one mole of PPh_3. The heat of dissociation required is 124.1 kJ mol^{-1}. The following endothermic peak at ca. 300 °C confirms the evolution of another CO with an enthalpy change of 12.2 kJ mol^{-1}

$$Cr(CO)_5(PPh_3) \xrightarrow{160\text{-}280\,^\circ C} [Cr(CO)_3] + 2CO + PPh_3$$

$$\Delta H = 124.1 \text{ kJ mol}^{-1}$$

$$[Cr(CO)_3] \xrightarrow{280\text{-}420\,^\circ C} [Cr(CO)_2] + CO$$

$$\Delta H = 12.2 \text{ kJ mol}^{-1}$$

$Mo(CO)_5(PPh_3)$

Thermogravimetric analysis

Figure 3 shows a weight loss at ca. 145 °C which can be related to the evolution of one mole of CO (obs., 6.6%; calc., 5.7%) which is followed immediately by the elimination of another mole of CO at ca. 180 °C (obs., 7.6%; calc., 5.7%). A high rate of weight loss is subsequently observed at ca. 200 °C and is probably due to the expulsion of one mole of PPh_3 (obs., 51.8%; calc., 52.6%). Evolution of three moles of CO occurs over two decomposition steps at ca. 310 °C and 650 °C (obs., 15.2%; calc., 17.0%).

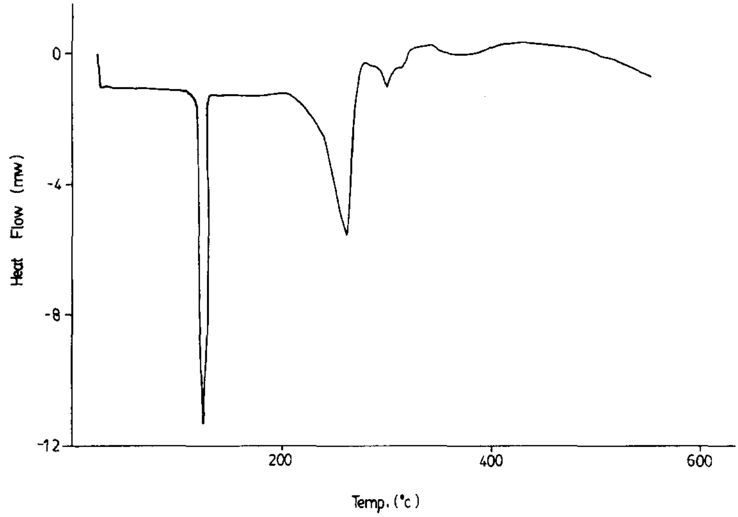

Fig. 2. DSC curve of $Cr(CO)_5(PPh_3)$.

The weight of the residue at 950 °C corresponds to Mo metal (obs., 18.9%; calc., 19.2%).

Differential scanning calorimetry

As shown in Fig. 4, the complex melts at 138 °C. The expulsion of the first CO may have overlapped with the melting process and is probably very labile. The enthalpy change for these overlapping processes is established to be 33.1 kJ mol^{-1}. The next CO requires 7.0 kJ mol^{-1} to dissociate as

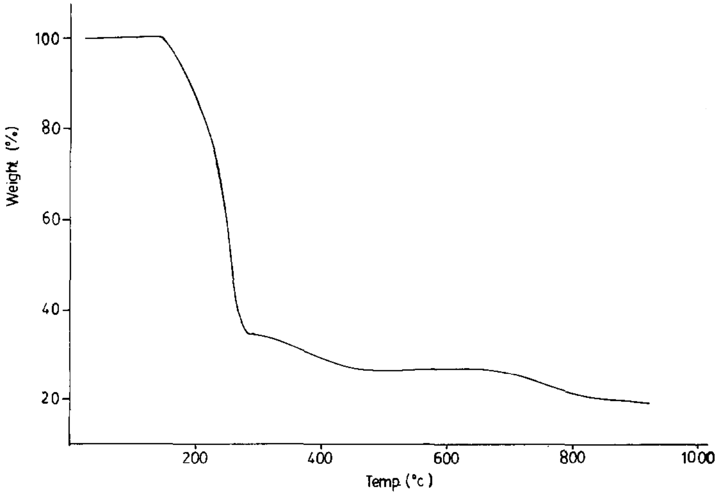

Fig. 3. TG curve of $Mo(CO)_5(PPh_3)$.

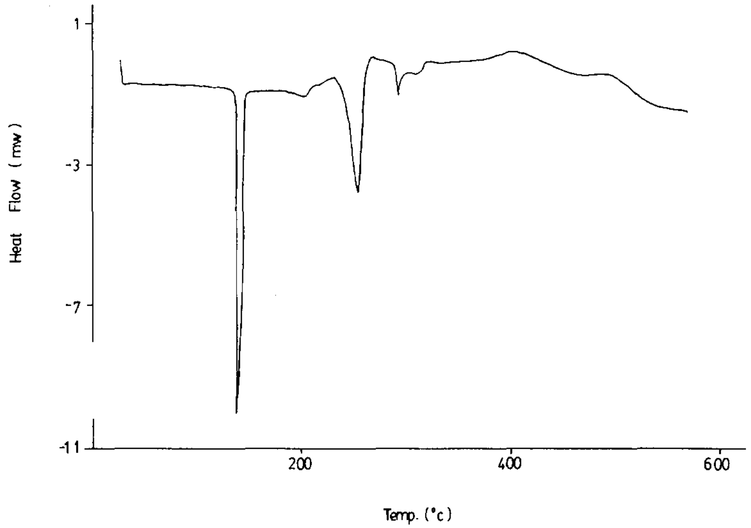

Fig. 4. DSC curve of $Mo(CO)_5(PPh_3)$.

indicated by the endothermic peak at ca. 180 °C. Such a low enthalpy value may imply an extreme labile expulsion of the ligand. The endothermic peak at ca. 240 °C ($\Delta H = 89.7$ kJ mol^{-1}) corresponds to the cleavage of one mole of PPh_3. The loss of the remaining three CO ligands occurs over two stages. A small endothermic peak at ca. 290 °C with the enthalpy 49 kJ mol^{-1} is responsible for the first step. The second stage occurs above 600 °C which is not shown in the DSC thermogram

$$Mo(CO)_5(PPh_3) \xrightarrow{140\text{-}180\,^\circ C} [Mo(CO)_4(PPh_3)] + CO$$

$\Delta H = 33.1$ kJ mol^{-1} (plus melting)

$$[Mo(CO)_4(PPh_3)] \xrightarrow{140\text{-}180\,^\circ C} [Mo(CO)_3(PPh_3)] + CO$$

$\Delta H = 7.0$ kJ mol^{-1}

$$[Mo(CO)_3(PPh_3)] \xrightarrow{200\text{-}300\,^\circ C} [Mo(CO)_3] + PPh_3$$

$\Delta H = 89.7$ kJ mol^{-1}

$$[Mo(CO)_3] \xrightarrow{300\text{-}900\,^\circ C} Mo + 3CO$$

$W(CO)_5(PPh_3)$

Thermogravimetric analysis

The complex decomposes at ca. 170 °C corresponding to the dissociation of PPh_3 (obs., 43.4%; calc., 44.9%) (Fig. 5). The subsequent weight loss suggests a concurrent elimination of all the five CO ligands (obs., 26.9%;

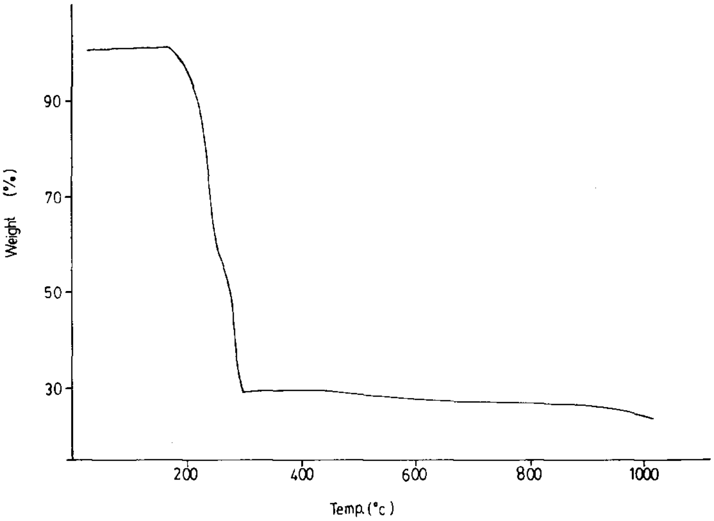

Fig. 5. TG curve of $W(CO)_5(PPh_3)$.

calc., 24.0%). The percentage weight of the residue corresponds to W metal (obs., 29.7%; calc., 29.6%).

Differential scanning calorimetry

Figure 6 indicates that the complex melts at 147 °C ($\Delta H = 33.3$ kJ mol^{-1}). The endothermic peak at ca. 270 °C is probably due to the elimina-

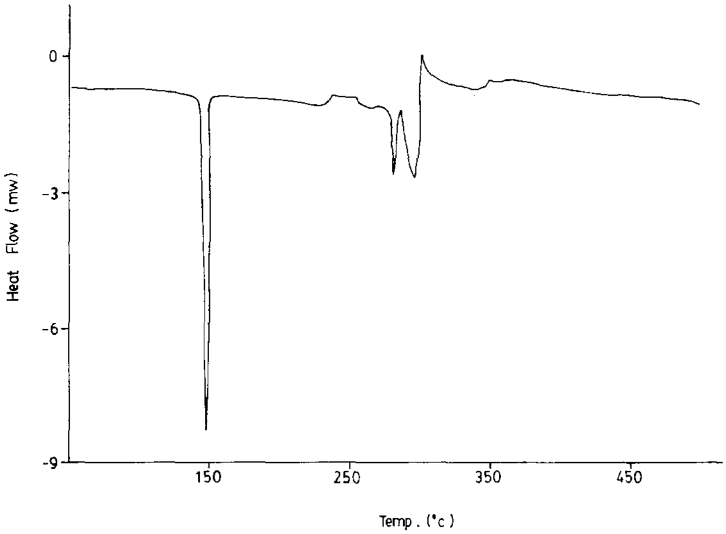

Fig. 6. DSC curve of $W(CO)_5(PPh_3)$.

tion of PPh_3 ($\Delta H = 8.9$ kJ mol^{-1}). The expulsion of the five CO ligands is represented by the endothermic peak at ca. 260–300 °C with an enthalpy change of 38.7 kJ mol^{-1}

$$W(CO)_5(PPh_3) \xrightarrow{170-260\,^\circ C} [W(CO)_5] + PPh_3$$

$$\Delta H = 8.9 \text{ kJ mol}^{-1}$$

$$[W(CO)_5] \xrightarrow{260-300\,^\circ C} W + 5CO$$

$$\Delta H = 38.7 \text{ kJ mol}^{-1}$$

DISCUSSION

The three compounds $Cr(CO)_5(PPh_3)$, $Mo(CO)_5(PPh_3)$ and $W(CO)_5(PPh_3)$ show different patterns of decomposition. The differences in the thermal behaviour of these complexes may be attributed to a combination of factors such as the relative M–CO and M–PPh_3 bond strengths, steric effects, σ- and π-bonding properties of the ligands and the charge density of the metals. Recent articles by Hoff and coworkers [4,5,24,25] and Connor and coworkers [6,26,27] have clearly demonstrated such complexities. The observed decompositions are further complicated by overlapping reactions.

The Cr complex is found to undergo concurrent decomposition in the first step which involves the elimination of two CO ligands and PPh_3. The TG and DSC analyses do not allow the sequence of the elimination step to be determined. In contrast, the TG and DSC analyses of the Mo complex enable the stepwise elimination of CO and PPh_3 to be clearly discernible. The Mo-bound CO appears to be more labile than its counterpart in the Cr complex. The fact that PPh_3 and CO possess comparable binding strength is not unexpected. Workulich and Atwood [28] examined the quantitative reactive ordering of the ground state free energies of similar pentacarbonyl chromium derivatives and found that PPh_3 binds to the metal with nearly the same energy as CO despite the marked differences in their electronic and steric properties. Nolan et al. [4], in studying the complexes fac-$L_3Mo(CO)_3$ also support this view.

Apparently unique is the decomposition sequence in the W complex when the phosphine is cleaved prior to the carbonyls. The bulkiness of PPh_3, with a cone angle of 150° [29], probably plays a major role in its lability. The notorious strength of the W–CO bond as compared with the Cr and Mo analogues [13,30–34] is in full accord with our observations. However, it must be added that the recorded enthalpy change of 8.9 kJ mol^{-1} for the W–PPh_3 bond cleavage is unexpectedly low. This value may not necessarily reflect the actual strength of the W–P bond, because in the present situation, the enthalpy change is complicated by the possible volatilisation of the species $W(CO)_5(PPh_3)$ and $[W(CO)_5]$, and the heat change involving the vaporisation of PPh_3. Al-Takhin et al. [26] presented an adequate description of these factors in their microcalorimetric study on the same complex. Our study indicated a complete stripping of ligands below 350 ° C with a residual weight corresponding to W metal (Fig. 5). This is consistent with the work performed by Al-Takhin et al. [26] but contrasts with our earlier observation on the bis(diphenylphosphino)methane substituted tungsten carbonyl [19]. As Figs. 1 and 3 indicate, complete elimination of the ligands is also observed in the Mo complex, but not in the Cr sample. Interestingly, these observations are in agreement with those of Lewis et al. [13] on the metal hexacarbonyls using prolonged laser pyrolysis.

Our earlier study on $M(CO)_5(dppm)$ (where M = Cr, Mo, W; dppm = bis(diphenylphosphino)methane) [19] suggested an initial loss of a CO ligand from all the three complexes. Such a pattern may be explained by the probable formation of a stable intermediate chelate, $M(CO)_4(\eta^2\text{-dppm})$. The present complexes $M(CO)_5(PPh_3)$ apparently display some irregularities in their breakdown. Such differences can be understood in terms of the exclusive unidentate nature of PPh_3, hence precluding the formation of a stable tetracarbonyl intermediate. The thermal breakdown of the $M(CO)_5(PPh_3)$ complexes may therefore show a more sensitive dependence on the steric and electronic nature of the metal and ligand.

CONCLUSIONS

Thermodynamic data obtained from more conventional gas-phase and solution techniques are complex but invaluable. The use of TG and DSC in the investigation of metal carbonyls is still in its infancy. Although they may not provide a direct measurement of the bond energies, the techniques offer an advantage as a means of investigation of the pattern of a sequential decomposition of an organometallic entity and its associated enthalpy change. The present study demonstrated the influence of the metal and ligand on the decomposition of the Group 6 metal carbonyls. Further work on similar systems is in progress. It is hoped that, using metal carbonyls as models, a complementary relationship between these thermal techniques and other classical solution and gas-phase methods can be established.

ACKNOWLEDGEMENT

Financial support of this work by the National University of Singapore (RP 30/85 and RP 37/84) is gratefully acknowledged.

REFERENCES

1 J.L. Goodman, K.S. Peters and V. Vaida, Organometallics, 5 (1986) 815.
2 J. Halpern, Acc. Chem. Res., 15 (1982) 238.
3 J.A. Connor, in B.F.G. Johnson (Ed.), Transition Metal Clusters, Wiley, New York, 1980, Chapter 5.
4 S.P. Nolan, R. Lopez de la Vega and C.D. Hoff, Organometallics, 5 (1986) 2529.
5 C.D. Hoff and S.P. Nolan, J. Organomet. Chem., 290 (1985) 365.
6 J.A. Connor, M.T. Zafarani-Moattar, J. Bickerton, N.I. El Saied, S. Suradi, R. Carson, G. Al Takhin and H.A. Skinner, Organometallics, 1 (1982) 1166.
7 B. Pilcher and H.A. Skinner, in F.R. Hartley and S. Patai (Ed.), The Chemistry of the Metal–Carbon Bond, Wiley, New York, 1982, Chapter 2.
8 M.J. Calhorda, M.A.A.F. de C.T. Carrondo, A.R. Dias, A.M.T.S. Domingos, J.A. Martinho-Simoes and C. Teixeira, Organometallics, 5 (1986) 660.
9 L.E. Manzu and C.A. Tolman, J. Am. Chem. Soc., 97 (1975) 1955.
10 W. Partenheimer, Inorg. Chem., 11 (1972) 743.
11 J.D. Atwood, M.J. Wovkulich and D.C. Sonnenberger, Acc. Chem. Res., 16 (1983) 350.
12 D.L.S. Brown, J.A. Connor, C.P. Demain, M.L. Lenng, J.A. Martinho-Simoes, H.A. Skinner and M.T. Zafarani-Moattar, J. Organomet. Chem., 142 (1977) 321.
13 K.E. Lewis, D.M. Golden and G.P. Smith, J. Am. Chem. Soc., 106 (1984) 3905.
14 H.S.O. Chan and J.R. Lusty, J. Therm. Anal., 30 (1985) 25.
15 J.R. Lusty, H.S.O. Chan and J. Peeling, Transition Met. Chem., 8 (1983) 343.
16 G. D'Ascenzo and T. Bica, Thermochim. Acta, 18 (1977) 301.
17 T.J. Cardwell, D.J. Desarro and P.C. Uden, Anal. Chim. Acta, 85 (1976) 415.
18 D.N. Sokolov and G.N. Nesterenko, Zh. Anal. Khim., 30 (1975) 2377.
19 H.S.O. Chan, T.S.A. Hor, J.R. Lusty, T.C. Chong and C.S.M. Chiam, J. Therm. Anal., (1987) in press.
20 D.J. Darensbourg and T.L. Brown, Inorg. Chem., 7 (1968) 1679.
21 S.O. Grim, D.A. Wheatland and W. McFarlane, J. Am. Chem. Soc., 89 (1967) 5573.
22 T.S.A. Hor, J. Organomet. Chem., 319 (1987) 213.
23 T.A. Magee, C.N. Mattews, T.S. Wang and J.H. Wotiz, J. Am. Chem. Soc., 83 (1961) 3200.
24 C.D. Hoff, J. Organomet. Chem., 282 (1985) 201.
25 C.D. Hoff and J.T. Landrum, J. Organomet. Chem., 282 (1985) 215.
26 G. Al-Takhin, J.A. Connor, G. Pilcher and H.A. Skinner, J. Organomet. Chem., 265 (1984) 263.
27 J.A. Connor, J.A. Martinho-Simoes, H.A. Skinner and M.T. Zafarani-Moattar, J. Organomet. Chem., 179 (1979) 331.
28 M.J. Workulich and J.D. Atwood, J. Organomet. Chem., 184 (1979) 77.
29 C.A. Tolman, Chem. Rev., 77 (1977) 313.
30 D.S. Barnes, G. Pilcher, D.A. Pittam, H.A. Skinner, D. Todd and Y. Virmani, J. Less-Common Met., 36 (1974) 177.
31 D.J. Darensburg, Adv. Organomet. Chem., 21 (1982) 113; and references therein.
32 M.O. Albers and N.J. Coville, Coord. Chem. Rev., 53 (1984) 227; and references therein.
33 G. Pilcher, M.J. Ware and D.A. Pittam, J. Less-Common Met., 42 (1975) 223.
34 F.A. Adedeji, J.A. Connor, C.P. Demain, J.A. Martinho-Simoes, H.A. Skinner and M.T. Zafarani-Moattar, J. Organomet. Chem., 149 (1978) 333.