DRIFTS and Optical Microscopic Study of the Solventless Reaction between (η^5-C_5H_5)M(CO)$_3$CH$_3$ (M = Mo, W) and L (L = P(p-FC$_6$H$_4$)$_3$, P(C$_6$H$_5$)$_3$)

Muhammad D. Bala, Asheena Budhai, and Neil J. Coville*

Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, Johannesburg 2050, South Africa

Received December 18, 2003

The reaction between solid (η^5-C_5H_5)M(CO)$_3$CH$_3$ and solid phosphines is shown to occur in the melt phase (optical microscopy), and a DRIFTS study of the melt reveals a well-behaved reaction following pseudo-first-order kinetics.

Introduction

Solvent-free synthesis has received increased attention, due partly to environmental concerns[1] but also because of the potential novel products and mechanisms that can be generated when reactions are conducted in the absence of solvents.[2] While solventless synthesis has been well studied in organic chemistry[3,4] and materials science,[5] the study of *solvent-free organometallic reactions* is still relatively unexplored and the potential this method has in organometallic synthesis has yet to be fully established.[6]

In a continuation of our studies on organometallic transformations in the absence of solvents, we recently reported on the migratory insertion of (η^5-C_5H_5)M(CO)$_3$-Me (**1**: M = Mo, W) in the presence of phosphines (Scheme 1). Some of the reactions appeared to occur in the solid state.[7] However, it is difficult to imagine a mechanism that would allow for an insertion reaction between two solids. To further explore this reaction, we have now studied the reaction using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and optical microscopy.

DRIFTS is a technique that can be used to study chemical reactions when the reactants are in the form of powders or crystalline solids and is thus well suited to the study of the migration/insertion reaction under investigation.[8]

The DRIFTS technique offers the following advantages: (i) in situ measurements, (ii) facile data collection, (iii) the ability to work under inert reaction conditions, (iv) the ability to work in temperature regimes between 25 and 500 °C, (v) the ability to perform reactions under pressure, and (vi) the use of small samples of reagents. As will be shown in this study, DRIFTS can also be used to study reactions in the melt phase.

In particular, our study has thus entailed the reaction of solid phosphines (e.g. P(p-FC$_6$H$_4$)$_3$) with (η^5-C_5H_5)M(CO)$_3$CH$_3$ (M = Mo, W) at temperatures *below the melting points of the reactants and products*. An optical microscopic study was used to monitor the physical changes as the reaction progressed.

Experimental Section

The metal complexes (η^5-C_5H_5)M(CO)$_3$Me (M = Mo, W) were prepared by adaptation of literature procedures,[9] and the new products (η^5-C_5H_5)M(CO)$_2$P(p-FC$_6$H$_4$)$_3$(COMe) (M = Mo, W) were characterized by elemental analysis and IR and NMR spectroscopy.

Details on the equipment and methods used for analytical and spectroscopic studies (DRIFTS, NMR, DSC, etc.) and the results from such studies are available as Supporting Information.

DRIFTS Studies. The samples for DRIFTS studies were prepared by mechanical grinding all reactants to a fine powder (40−80 μm particle size) using a pestle and mortar. Typically 1−2 wt % of the metal complex (η^5-C_5H_5)M(CO)$_3$Me (M = Mo, W) in KBr (as a diluent) was ground together. A similar weight percentage of the phosphine diluted with KBr was also ground together. No reaction occurred between KBr and either of the reactants due to the grinding process.[10] Similar results were obtained when NaCl and Al$_2$O$_3$ were used as diluents.

The finely ground phosphine/KBr mixture was first loaded into the DRIFTS cell and measured as the background, and then the separately ground complex/KBr and phosphine/KBr mixtures were thoroughly mixed in the required molar ratio to give a homogeneous powder (no grinding). This homoge-

---

[1] Anastas, P. T.; Warner, C. *Green Chemistry, Theory and Practice*; Oxford University Press: London, 1998.

[2] (a) Cheng, L.; Coville, N. J. *Organometallics* **1996**, *15*, 867. (b) Coville, N. J.; Cheng, L. *J. Organomet. Chem.* **1998**, *571*, 149. (c) Coville, N. J.; Levendis, D. C. *Eur. J. Inorg. Chem.* **2002**, 3067.

[3] See, for example, the following reviews: (a) Paul, I. C.; Curtin, D. Y. *Acc. Chem. Res.* **1973**, *6*, 217. (b) Toda, F. *Acc. Chem. Res.* **1995**, *28*, 480. (c) Metzger, J. O. *Angew. Chem., Int. Ed.* **1998**, *37*, 2975. (d) Toda, F.; Tanaka, K. *Chem. Rev.* **2000**, *100*, 1025. (e) Cave, G. W.; Raston, C. L.; Scott, J. L. *Chem. Commun.* **2001**, 2159.

[4] Patil, A. O.; Curtin, D. Y.; Paul, I. C. *J. Am. Chem. Soc.* **1984**, *106*, 348.

[5] (a) Thadhani, N. N. *Prog. Mater. Sci.* **1993**, *37*, 117. (b) Moore, J. J.; Feng, H. J. *Prog. Mater. Sci.* **1995**, *39*, 243.

[6] Kaupp, G.; Schmeyers, J.; Boy, J. *Chemosphere* **2001**, *43*, 55.

[7] Adeyemi, O. G.; Coville, N. J. *Organometallics* **2003**, *22*, 2284.

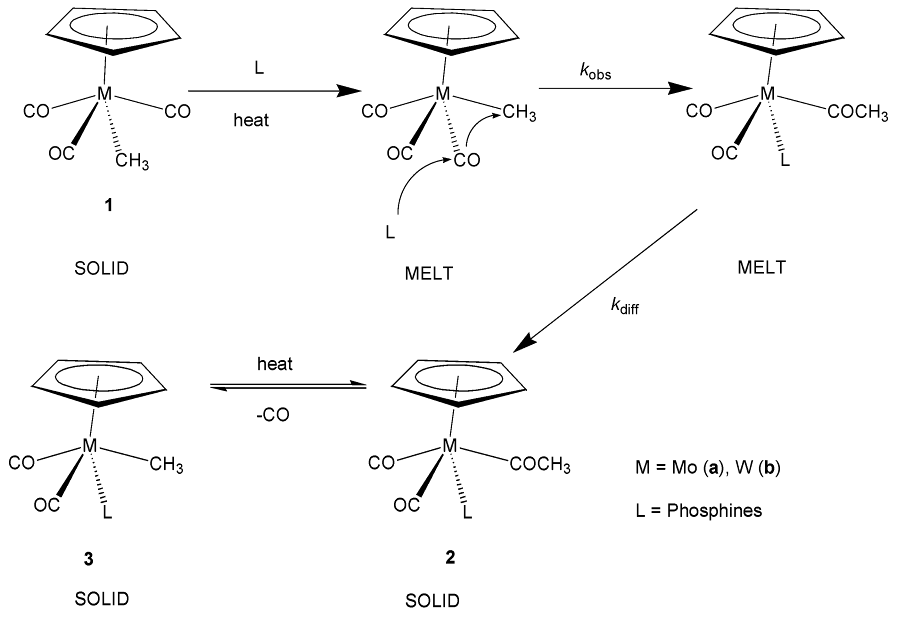
[8] (a) Fuller, E. L.; Smyre, N. R. *Appl. Spectrosc.* **1990**, *44*, 451. (b) Allen, T. J. *Vibr. Spectrosc.* **1992**, *3*, 217. (c) Ferraro, J. R.; Rein, A. J. Applications to Chemical Systems. In *Fourier Transform Spectroscopy*; Ferraro, J. R., Basile, L. J., Eds.; Academic Press: Orlando, FL, 1985; Vol. 4, p 253. (d) Krishnan, K. In *Fourier Transform Infrared Spectroscopy, Industrial Chemical and Biochemical Applications*; Theophanides, T., Ed.; D. Reidel: Dordrecht, The Netherlands, 1984; p 148. (e) Korte, E. H.; Röseler, A. In *Infrared and Raman Spectroscopy, Methods and Applications*; Schrader, B., Ed.; Wiley-VCH: Weinheim, Germany, 1995; p 598. (f) Ryczkowski, J. *Catal. Today* **2001**, *68*, 263.

[9] Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104.

[10] Braga, D.; Maini, L.; Polito, M.; Grepioni, F. *Chem. Commun.* **2002**, 2302.

10.1021/om0343869 CCC: $27.50

Scheme 1. Mechanism of the Migratory-Insertion Reaction



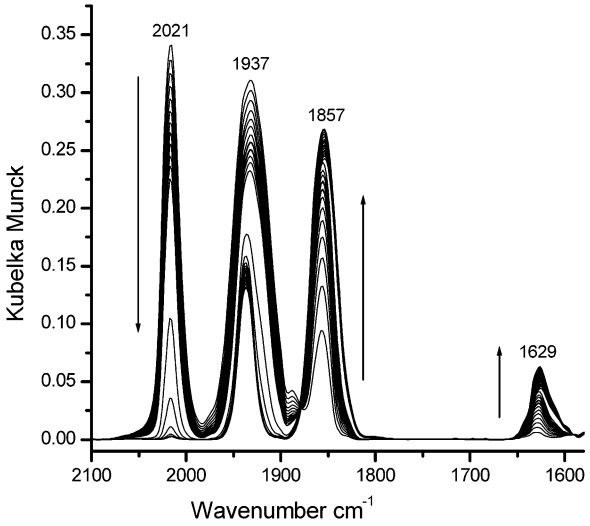


Figure 1. DRIFTS study of the reaction of (η^5-C_5H_5)W(CO)$_3$CH$_3$ with P(p-FC_6H_4)$_3$ at 60 °C (M:P 1:10 mol/mol).

neous mixture was then loaded into the DRIFTS cell and an initial IR spectrum recorded. The heating control was then adjusted to the required temperature (40−60 °C) and the FTIR program set to record repeated spectra (at preset time intervals). Reactant peaks decreased in intensity, while simultaneously new peaks associated with product formation were formed. The rate of disappearance of reactant peaks was monitored by the disappearance of the CO absorption at ca. 2020 cm^{-1}.

A typical set of data for the reaction is presented in Figure 1. As can be seen, the raw data show good behavior. Spectral kinetic information was extracted from the raw data. Figure 2 illustrates a plot of reactant conversion with time at 40 and 60 °C (reaction of (η^5-C_5H_5)M(CO)$_3$CH$_3$ with P(p-FC_6H_4)$_3$; M:P molar ratio of 1:10).

If it is assumed that the first part of the reaction at 40 °C and the reactions at 60 °C occur via a first-order rate law (i.e. the first 15 min of the reaction), then the plots shown in Figure 3 are obtained.

Rate constants for **1** were calculated for a range of reaction conditions (40−60 °C, varying reactant ratios, Mo and W), and the data are presented in Table 1.

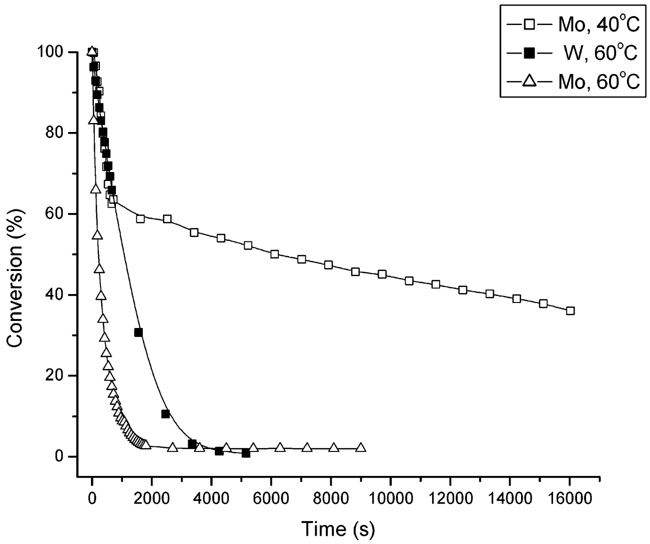


Figure 2. Comparison of rates of conversion to product as a function of time for the reaction of (η^5-C_5H_5)Mo(CO)$_3$CH$_3$ with P(p-FC_6H_4)$_3$ at 40 and 60 °C (M:P 1:10 mol/mol).

Arrhenius plots based on the data in Table 1 gave the calculated activation energies for the reaction.

Optical Microscopy Study. A homemade glass heating device with a dome for studies under an inert atmosphere, precalibrated with crystals of known melting points, was used for the study.[11] Attached above this cell was an optical microscope fitted with a digital camera. Crystals or fine powders of the reactants were placed on the glass surface. The heating device was then adjusted to heat at a certain rate to a preset temperature, while changes in the reactants were monitored and recorded on a PC monitor attached to the camera. Results from this study are presented in Figure 4.

Attempts were made to monitor the reaction by spreading of the reactants on KBr (in CH_2Cl_2; followed by solvent removal). However, difficulty was experienced in monitoring the reaction under the optical microscope, and this approach was not pursued further.

---

[11] Bogadi, R.; Levendis, D. C.; Coville, N. J. *J. Am. Chem. Soc.* **2002**, *124*, 1004.

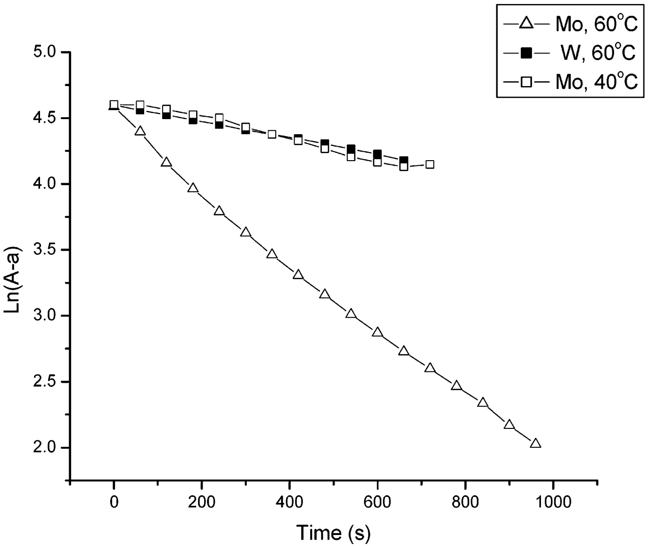


Figure 3. First-order plots of the reaction of (η^5-C_5H_5)M(CO)$_3$-CH_3 with P(p-FC_6H_4)$_3$ at a 1:10 M:P molar ratio.

Table 1. Data for the Reaction of (η^5-C_5H_5)M(CO)$_3$$CH_3$ with P(p-FC_6H_4)$_3$ Monitored by in Situ DRIFTS

M	temp, °C	M:P mol/mol	time,[a] s	$10^{-4}k$, s^{-1}	conversn, %[b]
Mo	40	1:1	1500	5.31	77
	50	1:1	2160	6.36	84
	60	1:1	1500	20.3	85
	40	1:10	1620	7.87	41
	50	1:10	2520	9.38	83
	60	1:10	1500	25.2	96
W	40	1:1	1500	7.05	50
	40	1:5	2520	3.94	35
	40	1:10	2160	2.33	35
	50	1:10	2820	2.52	44
	60	1:10	2460	7.59	89

[a] Period of reaction within which the first-order rate law was applicable. Note that all the systems attained 99% conversion over extended reaction periods. [b] Determined by DRIFTS.

Results and Discussion

The DRIFTS technique allowed the progress of the reaction of (η^5-C_5H_5)M(CO)$_3$$CH_3$ with solid phosphines (e.g. P(p-FC_6H_4)$_3$) to be monitored. Typical raw data for the reaction of (η^5-C_5H_5)W(CO)$_3$$CH_3$ with P(p-FC_6H_4)$_3$ at 60 °C (a temperature well below the melting points of the reactants) is presented in Figure 1. The reactant can be seen to be consumed (peak at 2021 cm^{-1}) as the product forms (peaks at 1857 and 1629 cm^{-1}). The peak at 1937 cm^{-1} results from both product and reactant contributions. The data for the reaction at 60 °C (1:10 ratio) has been plotted in Figure 2. At 60 °C the reaction is well behaved and a 96% conversion occurred within the first 25 min. If first-order kinetics are assumed, the plot shown in Figure 3 can be obtained ($k = 25.2 \times 10^{-4}$ s^{-1}).

At 40 °C the conversion versus time plot shows that there are at least two distinct reactions that can be detected (Figure 2). The first part of the reaction is observed to occur within the first 15−30 min and obeys a first-order rate law (1:10 ratio; $k = 7.87 \times 10^{-4}$ s^{-1}, Figure 3, Table 1). This is followed by a deceleration in rate ($k = 3.37 \times 10^{-5}$ s^{-1}). At 40 °C, even after 5 h, only 63% of the reactants were converted to product.

Further results were obtained from reactions in which the temperature and mole ratio of reactants were varied, and the rate constants for the reactions are shown in Table 1. The following points should be noted.

(i) Reactions with Mo are faster than with W. However, rate constants are only 2−3 times greater. Activation energies (E_a) for the reactions are as follows: (η^5-C_5H_5)W(CO)$_3$$CH_3$/P($p$-$FC_6H_4$)$_3$, 50 kJ mol^{-1}; (η^5-C_5H_5)Mo(CO)$_3$$CH_3$/P($p$-$FC_6H_4$)$_3$, >60 kJ mol^{-1}.

(ii) At 1:1 and 1:10 ratios of reactants (M = Mo, W), the rate increases with temperature.

(iii) At 40 °C the reaction between (η^5-C_5H_5)W(CO)$_3$-CH_3 and P(p-FC_6H_4)$_3$ revealed a decrease in reaction rate with increasing reactant ratio.

(iv) The reaction between (η^5-C_5H_5)Mo(CO)$_3$Me and PPh_3 gave a rate constant of 4.34×10^{-5} s^{-1} (1:1 ratio, 40 °C), which is comparable to the value obtained in ex situ studies, as reported earlier (1.81×10^{-5} s^{-1}).[6] The difference could be due to experimental issues associated with small temperature differences relating to the different techniques. The data do suggest that the presence of KBr does not significantly affect the reaction.

(v) The conclusion of point iv is further suggested by reactions performed with other diluents (NaCl and Al_2O_3), in which similar rate constant variations, under similar reaction conditions, were noted (ca. 4×10^{-5} s^{-1}).

(vi) The latter result indicates that rapid in situ data can readily be obtained by the DRIFTS technique, in agreement with data obtained by less accurate and more time-consuming approaches.

To rationalize the kinetic data and determine a possible mechanism for the reaction, an optical microscopy study was initiated. Remarkably, the reaction of (η^5-C_5H_5)W(CO)$_3$$CH_3$ with P(p-FC_6H_4)$_3$ was found to commence at temperatures of about 41 °C, a temperature far below that of the melting points of the reactants ((η^5-C_5H_5)W(CO)$_3$$CH_3$, mp 142 °C; P($p$-$FC_6H_4$)$_3$, mp = 80 °C). DSC thermographs of reactant mixtures in the absence of diluent do indicate a lowering of the melting points, in line with this effect (see the Supporting Information).

Figure 4 shows photographs of the reaction as a function of time. Figure 4a shows the reactants at room temperature prior to reaction. The reactants have been arranged such that separated and contiguous reagents can be seen. When the samples are heated, at just over 40 °C, melting rapidly occurs for the reactants in contact with each other but not for the reactants separated from each other (Figure 4b,c). Progression of the reaction resulted in a consumption of reactants and crystallization of material out of the melt (Figure 4d). The overall appearance was that of a solid to solid reaction. IR and NMR analyses confirmed the formation of the product (η^5-C_5H_5)W(CO)$_2$(P(p-FC_6H_4)$_3$)COCH$_3$ in the reaction. Similar results were obtained for the other reactions.

A mechanism for the reaction can be offered. Physical contact between the two reactants (η^5-C_5H_5)M(CO)$_3$$CH_3$ and P(p-FC_6H_4)$_3$ results in formation of a eutectic solution with a melting point lower than that of the separate reactants.[12] This melt permits intimate mixing

---

(12) (a) Rothenberg, G.; Downie, A. P.; Raston, C. L.; Scott, J. L. *J. Am. Chem. Soc.* **2001**, *123*, 8701. (b) Brown, W. E.; Dollimore, D.; Galwey, A. K. In *Comprehensive Chemical Kinetics*; Bamford, C. H., Tipper, C. F. H., Eds.; Elsevier: Amsterdam, 1980; Vol. 22, p 247.

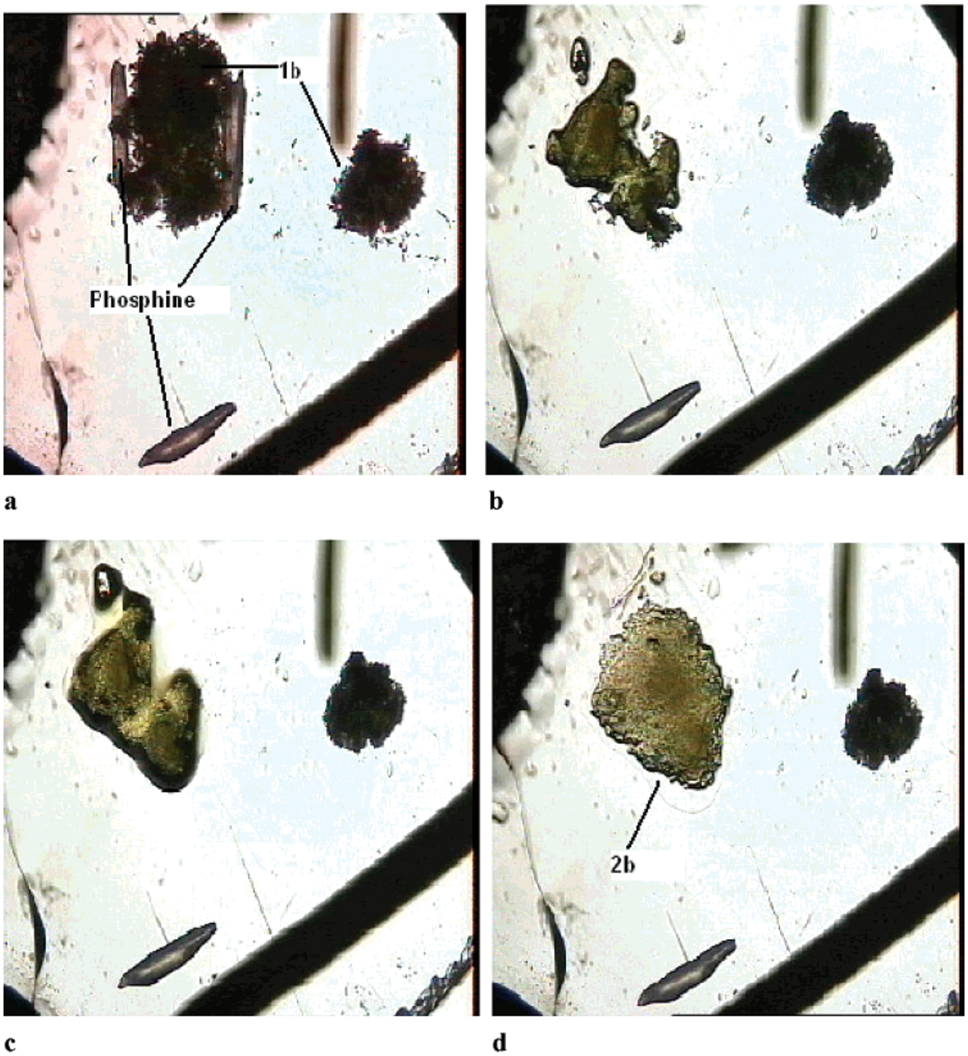


Figure 4. Interface melting in the reaction of (η^5-C_5H_5)W(CO)$_3$CH$_3$ with P(p-FC$_6$H$_4$)$_3$ at 40 °C: (a) room temperature; (b) 40 °C/1 min; (c) 40 °C/2 min; (d) 40 °C/10 min.

of reagents. At the reaction temperature (>40 °C) the methyl migration/insertion occurs *in the melt* by the classical mechanism that occurs in the solution phase (as indicated by kinetic studies).

The results thus explain the data obtained when the reaction was monitored ex situ[7] and implies that these earlier reactions also took place in the melt. The excellent kinetic data for what appears to be a solid-state reaction can now be rationalized.

The actual initiation of the reaction, i.e., the method by which the reactants contact each other, is still open to speculation. The reagents have low melting points and high vapor pressures (all starting materials sublime), and this could provide a method for additional reactant contact at a surface.

However, a complicating issue is the precipitation of the product from the melt. The optical microscopy study clearly shows the crystallization of product *in the low-temperature reactions* (Figure 4d). This is also indicated by the change in kinetics with time at 40 °C (see above) that indicates a diffusion-controlled reaction.

The effect of diffusion was also noted for the reaction of (η^5-C_5H_5)W(CO)$_3$CH$_3$ with different amounts of P(p-FC$_6$H$_4$)$_3$ at low temperature. The unexpected lowering of reaction rate with increased ratio of P(p-FC$_6$H$_4$)$_3$ can be explained by the lowered ability to form a melt, resulting in the greater difficulty of the W complex to make intimate contact with the phosphine.

Similar results were obtained for reactions carried out with PPh$_3$.

Finally, it is worth noting that initial results from an ongoing study in our laboratory of CO substitution reactions by phosphines (L = PPh$_3$, P(p-OMePh)$_3$) on Mn(CO)$_4$(PPh$_3$)Br also indicates reactant *interface* melting prior to reaction and generation of the product Mn(CO)$_3$(PPh$_3$)(L)Br.[13] This implies that this type of reaction is quite general, with implications for many other so-called “solid−solid” reactions.[14]

Conclusions

The insertion/migration reaction described above reveals that a combination of DRIFTS and optical

---

[13] Manzini, S. S.; Coville, N. J. *Inorg. Chem. Comm.*, in press.

[14] (a) Toda, F.; Yagi, M.; Kiyoshige, K. *J. Chem. Soc., Chem. Commun.* **1988**, 958. (b) Toda, F.; Tanaka, K.; Iwata, S. *J. Org. Chem.* **1989**, *54*, 3007. (c) Toda, F.; Tatsuya, S. *J. Chem. Soc., Perkin Trans. 1* **1989**, 209. (d) Toda, F.; Takumi, H.; Masafumi, A. *J. Chem. Soc., Chem. Commun.* **1990**, 1270. (e) Goud, B. S.; Desiraju, G. R. *J. Chem. Res., Synop.* **1995**, 244. (f) Im, J.; Kim, J.; Kim, S.; Hahn, B.; Toda, F. *Tetrahedron Lett.* **1996**, *38*, 451. (g) Schmeyers, J.; Toda, F.; Boy, J.; Kaupp, G. *J. Chem. Soc., Perkin Trans. 2* **1998**, 989. (h) Kaupp, G.; Schmeyers, J.; Kuse, A.; Atfeh, A. *Angew. Chem., Int. Ed.* **1999**, *38*, 2896.

microscopy studies can provide information on environmentally benign solventless reactions. The DRIFTS data were collected for a reaction that comprises a mixture of KBr together with a melt of the organometallic reactants, and the DRIFTS technique allowed for the facile collection of kinetic data. This implies that DRIFTS can be used to monitor reactions not only in the solid phase but also in the liquid (melt) phase, extending the range of the technique.

In this specific example, solventless reactions of phosphines with transition-metal cyclopentadienyl carbonyls to give high yields of pure products have been demonstrated.

Acknowledgment. We wish to thank the NRF, THRIP, and the University of the Witwatersrand for financial support.

Supporting Information Available: Text giving experimental results and a figure giving DSC thermograms. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0343869