DOI: 10.1002/ejic.200501049

Aminoethyl-Functionalized Cyclopentadienyliridium Complexes: Photochemical C–H Activation and Carbonylation of Cycloalkanes

Pek Ke Chan,[a] Weng Kee Leong,*[a] Karl I. Krummel,[b] and Marc V. Garland*[b]

Keywords: Carbonylation / C–H activation / Cyclopentadienyl ligands / Iridium / Photochemistry

The photochemical C–H activation of cycloalkanes by aminoethyl-functionalized cyclopentadienyliridium complexes proceeds in a broadly similar way to that for their unfunctionalized analogues. In a carbon monoxide atmosphere, there is evidence that carbonylation to form the carboxaldehyde occurred with both systems. In situ infrared spectroscopic studies on these reactions allow the identification of several species present in low concentrations in the reaction mixture.

Introduction

UV initiated photodissociation of CO or H_2 from group-9 organometallic compounds of the type [CpMLL′] or [Cp*MLL′] (M = Ir, Rh; L = CO, PMe_3; L′ = CO, H_2) have been known to generate intermediates that are capable of activating the otherwise inert C–H bonds in hydrocarbon solvents.[1] This has stimulated much interest due to the plentiful supply of alkanes and the potential of using alkanes as chemical feedstocks for catalytic syntheses of organic molecules. Over the last two decades there have been several studies on the mechanism, kinetics, and thermodynamics of this activation process in solution, the gas phase, low-temperature matrices, and liquid noble gases.[1d,2] For $[Cp^XM(CO)_2]$ (Cp^X = Cp or Cp*; M = Ir or Rh), spectroscopic measurements have shown that the primary photoproduct is a coordinatively unsaturated 16-electron species $[Cp^XM(CO)]$ obtained by dissociation of a CO ligand. This species is extremely reactive and forms a solvent adduct complex $[Cp^XM(CO)\cdots S]$ before undergoing C–H activation to give the hydridoalkyl species $[Cp^XM(CO)(R)(H)]$.[2b,3]

Many functionalized cyclopentadienyl ligands containing side-chain donor groups (OR, NRR′, PRR′, $CH{=}CH_2$) are beginning to appear in the literature. In particular, we were interested in aminoethyl-functionalized cyclopentadienyl ligands because of their "hard-soft" combination of electron donors; the cyclopentadienyl ligand is known to stabilize transition metals in high as well as low oxidation states whereas the amino group favors coordination to metals in high oxidation states. Only weak interactions are anticipated to metals in low oxidation states, although these may be strengthened by the chelate effect.[4] As a result, aminoethyl-functionalized cyclopentadienyl ligands may be expected to behave as hemilabile ligands; under the conditions for the activation of hydrocarbons, the nitrogen donor on the side-arm of the aminoethyl-functionalized cyclopentadienyliridium complex may coordinate to the iridium center. This reversible coordination to a reactive metal center is of general interest in catalysis as it may stabilize a highly reactive, electronically and sterically unsaturated intermediate by weakly occupying the vacant coordination site until the actual substrate coordinates and replaces the amino group.[5] In this paper, we present the results of our study on the photolysis of $[Cp^*Ir(CO)_2]$ (**1b**), as well as its aminoethyl-functionalized analogue, in vacuo or under an argon or carbon monoxide atmosphere.

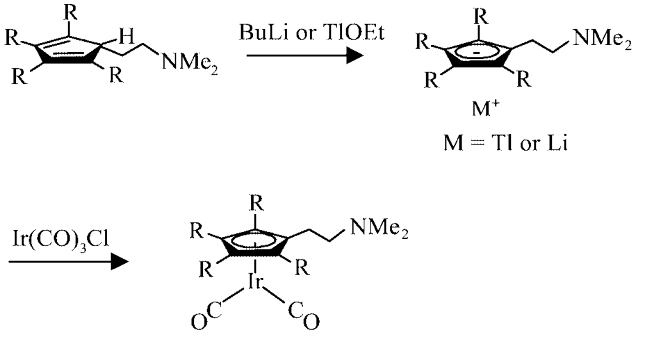
Results and Discussion

The aminoethyl-functionalized cyclopentadienyliridium complexes $[Cp^\wedge Ir(CO)_2]$ (**1c**) and $[Cp^{*\wedge}Ir(CO)_2]$ (**1d**; $Cp^\wedge$ = $C_5H_4CH_2CH_2NMe_2$ and $Cp^{*\wedge}$ = $C_5Me_4CH_2CH_2NMe_2$) were synthesized by an analogous route to that reported for $[CpIr(CO)_2]$ (**1a**; Scheme 1).[6]

The UV absorption spectrum of **1d** shows absorption maxima at about 210 and 280 nm. Upon UV irradiation of a degassed solution of **1d** in cyclohexane, the solution darkened slowly from yellow to orange-brown. Monitoring the photolysis by infrared spectroscopy showed initial formation only of the corresponding hydridoalkyl species **2d** (ν_{CO} = 1981 cm^{-1}), the CO stretching vibration of which is essentially identical to that of the [Cp*IrCO(Cy)(H)] analogue (ν_{CO} = 1981 cm^{-1} in cyclohexane).[7] As the photolysis progressed, a new species showing a carbonyl stretch at 1996 cm^{-1} in the infrared spectrum and a hydride resonance at δ = –15.7 ppm ($[D_8]$toluene) in the ^1H NMR spectrum was formed (Scheme 2). This was assigned to the dihydride

---

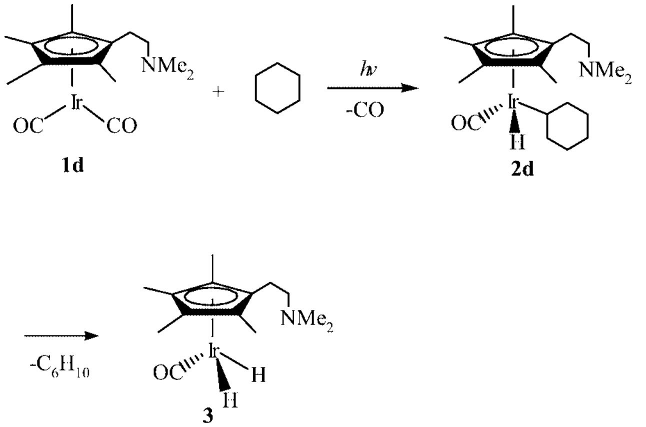
[a] Department of Chemistry, National University of Singapore,
3 Science Drive 3, Singapore 117543, Singapore
[b] Department of Chemical and Biomolecular Engineering, National University of Singapore,
4 Engineering Drive 4, Singapore 119260, Singapore



1c R = H
1d R = Me

Scheme 1.

complex **3** by comparison of its spectroscopic data with the analogue [Cp*Ir(CO)H$_2$] (ν_{CO} = 1996 cm^{-1} in cyclohexane; δ = –15.8 ppm in C$_6$D$_6$);[7,8] the latter was reported to form when **1b** was irradiated under a hydrogen atmosphere.[7]



Scheme 2.

Since our irradiation experiment was carried out in the absence of hydrogen gas, the formation of **3** may have resulted from β-hydrogen elimination of cyclohexene from **2d**. Indeed, cyclohexene was detected by GC-MS analysis of the reaction solution. Similar irradiation of **1c** in cyclohexane also resulted in the formation of the corresponding dihydride species, although in this case there appeared to be some decomposition during irradiation. Similar results could also be achieved in a shorter time by irradiation with a 266-nm laser; for **1c**, the ratio of **1c**/**2c**, as determined by the relative intensities of the CO absorbance, was 3.3 after 6 h of UV irradiation, while the ratio was 2.0 after irradiation with the laser for 45 minutes. We also found that with [(C$_5$H$_4$CH$_2$Ph)Ir(CO)$_2$] (**1e**), which has a benzyl group as the side-arm, a dihydride species was also obtained. It therefore appears that photolysis of the complexes carrying a side-arm results in the formation of dihydride complexes; this has not been reported to occur with [Cp*Ir(CO)$_2$] itself. The ^{1}H NMR spectrum of the reaction mixture also shows another hydride resonance at δ = –17.5 ppm, which could be due to intramolecular C–H activation of the amine group on the Cp ligand or CO insertion into the Ir–C bond to give the acyl species [Cp*^Ir(CO)(H)(COC$_6$H$_{11}$)].

Under a CO atmosphere (1 bar), the activation of **1d** in cyclohexane to form **2d** was slower and occurred with lower yield; the ratio of the absorbance of the CO stretch for **2d**/**1d** was 0.43 after 5 h under a CO atmosphere, and 1.4 after 2 h in vacuo. The same difference in ratios was observed for the activation of **1b** in cyclohexane to form **2b**; the ratio of (absorbance of) **2b**/**1b** was essentially constant at 0.65 after 30 min under a CO atmosphere, while it increased steadily from 1.03 at 30 min to 1.61 at 60 min in vacuo, although there were signs of decomposition in the latter on prolonged photolysis. Instead of **3**, the cluster [Ir$_4$(CO)$_{12}$] (**4**; ν_{CO} = 2029, 2069 cm^{-1}) was obtained together with **2d**; cluster **4** was also obtained from **1b** under similar conditions. Cluster **4** was not formed when a cyclohexane solution of **1d** was stirred under a CO atmosphere without irradiation. However, if the cyclohexane solution of **1d** was first irradiated, and then a CO atmosphere introduced, a mixture of **1d**, **2d**, and **4** was obtained; the changes in the relative intensities in the infrared spectra suggest that **3** is completely converted into **4** while **2d** is only partially converted into **4**. If this mixture was degassed and then subjected to irradiation, a mixture of **1d**, **2d**, and **3** was obtained. All these are summarized by the scheme and spectra given in Figure 1, and suggest that **4** is formed by the decomposition of **2d** and **3**, and that this is reversible.

$$\mathbf{1d} + C_6H_{12} \xrightarrow{h\nu} \mathbf{1d} + \mathbf{2d} + \mathbf{3} \underset{\text{degas, } h\nu}{\overset{\text{CO}}{\rightleftarrows}} \mathbf{1d} + \mathbf{2d} + \mathbf{4}$$

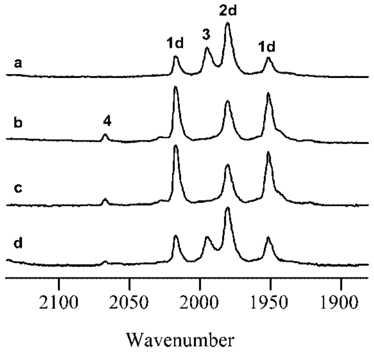


Figure 1. IR spectra of **1d** taken in cyclohexane: (a) after UV irradiation in vacuo for 6 h, followed by (b) stirring overnight under 1 atm of CO, (c) degassing and stirring overnight in vacuo, and (d) UV irradiation in vacuo for 3 h.

We confirmed the identity of **4** by an independent synthesis,[9] and also found that upon irradiation, a degassed suspension of **4** in cyclohexane in the presence of Cp*H or Cp*^H gave partial conversion to **1b** or **1d**, respectively, as identified by IR spectroscopy. Further irradiation of the reaction mixture containing **1b** and the starting materials resulted in the formation of the corresponding hydridoalkyl species **2b**; the yield of **2d** for the corresponding reaction was low. At the end of the 5 h irradiation, suspension of **4** in the reaction mixture was still observed, thus the low conversion rates may be attributed to the low solubility of **4** in cyclohexane.

In line with earlier findings that smaller rings show higher reactivity toward C–H activation,[1c,10] we found that the C–H activation of cyclopentane by **1d** was indeed more facile; the ratio of **2e**/**1d** (by absorbance) was 2.22 after 10 min, compared to a **2d**/**1d** ratio of 1.94 after the same period. These figures also indicate that the activation of **1d** is faster than that of **1b**. On stirring the resultant solution overnight under a CO atmosphere, both **2e** and **3** converted completely into **4** (Figure 2).

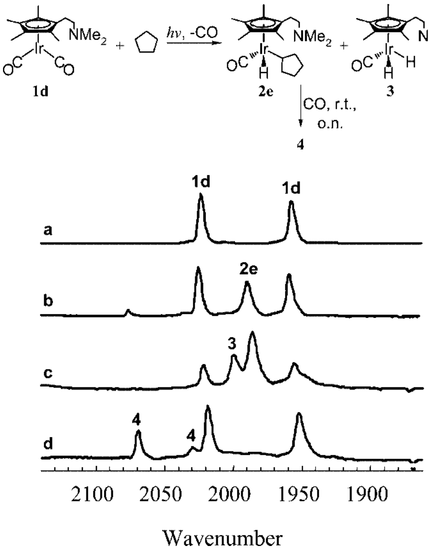
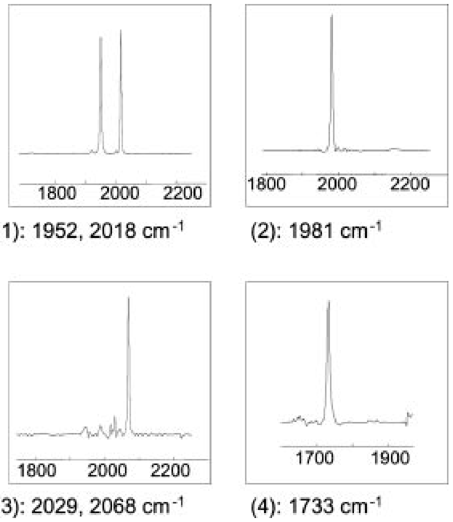


Figure 2. IR spectrum of **1d** in cyclopentane: (a) after stirring for 2 h under CO, followed by (b) 3 h UV irradiation under CO, (c) degassing and irradiation for 3 h in vacuo, and finally (d) stirring overnight under 1 atm of CO.

To gain further insight into the process, particularly with respect to the detection of compounds that we have hitherto not isolated or identified, we carried out in situ IR measurements on the C–H activation of cyclohexane, and used the band-targeted entropy minimization (BTEM) technique that one of us has developed for deconvolution of the data matrix.[11] The BTEM algorithm has been proven to be useful for picking up signals due to species that are present in low concentration, have low absorbance, are unstable, or have peaks that overlap with those due to other species.[11] The schematic diagram for the set-up used for the in situ IR measurements is shown below (Figure 3).

Measurements were made for both **1b** and **1d**; for each complex, spectra were collected at 5 min intervals, and a total of 232 spectra were collected.[12] For **1b**, the individual IR spectra of **1b**, **2b**, and **4**, in the CO stretching region (1650–2250 cm^{-1}) were recovered, together with the C=O stretch for cyclohexanecarboxaldehyde (Figure 4). Further confirmation of the aldehyde identity was obtained by NMR and GC-MS characterization. Formation of the corresponding carboxaldehyde in reactions carried out with cyclopentane was also observed by NMR spectroscopy. The carboxaldehyde could have been formed by carbonylation



(1): 1952, 2018 cm^{-1} (2): 1981 cm^{-1}

(3): 2029, 2068 cm^{-1} (4): 1733 cm^{-1}

Figure 4. Pure component IR spectra of individual species recovered from deconvolution of the IR spectra of the reaction mixture: (1) [Cp*Ir(CO)$_2$] (**1b**), (2) [Cp*Ir(CO)(H)(C$_6$H$_{11}$)] (**2b**), (3) [Ir$_4$(CO)$_{12}$] (**4**), and (4) C$_6$H$_{11}$CHO.

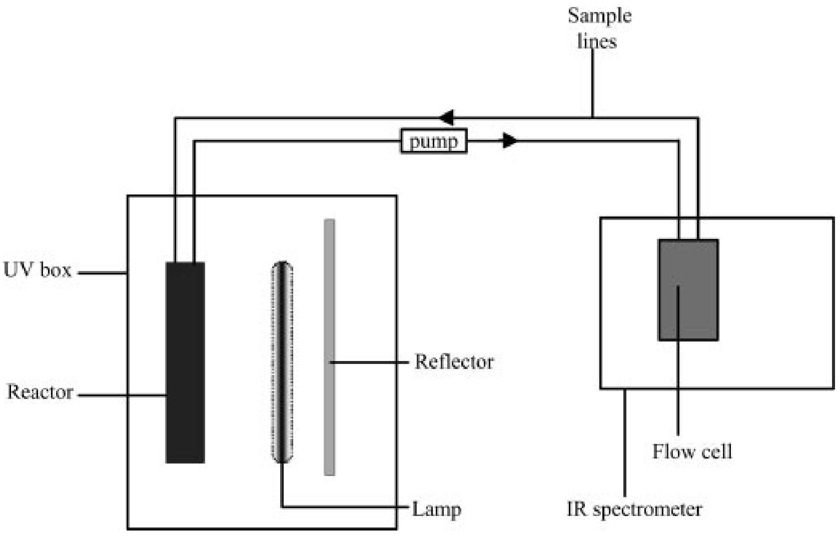


Figure 3. Schematic diagram of the set-up used for in situ IR measurements.

of the hydridoalkyl species followed by reductive elimination. Carbonylation of hydrocarbons catalyzed by group-9 transition metal complexes such as $[RhCl(CO)(PMe_3)_3]$ under UV irradiation has been reported,[13] but 18-electron Cp*Ir complexes have not been known to carbonylate hydrocarbons as it was believed that coordination of an incoming CO ligand would result in dissociation of the hydrocarbon.[14] A FAB-MS analysis of the reaction mixture yielded a fragment at *m*/*z* 267 in the positive-ion mode, and the ^{13}C NMR spectrum also shows a resonance at δ = 210.54 ppm, both of which suggest the presence of an acyl species, which may be the intermediate in the carbonylation reaction, although we have yet to confirm its identity.

We analyzed the yield of carboxaldehyde by GC-FID and found that UV irradiation of **1b** in cyclohexane in vacuo for one hour (absence of external CO source) afforded 0.9% of cyclohexanecarboxaldehyde (wrt [Ir]). When the photolysis was carried out under CO (1 bar) for the same length of time, the yield of aldehyde was 71.8%. So far, however, the yield is still far from catalytic. A high CO pressure may inhibit the initial CO dissociation from the dicarbonyliridium complex while favoring the insertion of CO into the Ir–C bond to form the putative $[Cp^*Ir(CO)(COC_6H_{11})(H)]$ acyl intermediate. Photolysis at various CO pressures (1.3 to 7.4 bars) was carried out but we did not find any significant trend in the aldehyde yield with CO pressure.

Conclusions

We have found that dicarbonylcyclopentadienyliridium complexes in which there is a side-arm carrying an amino group undergo photochemical C–H activation of alkanes in much the same way as the parent complexes without the side-arm. By employing in situ IR measurements and using iterative band-targeted entropy minimization to analyze the spectra, however, we have been able to detect the presence of many hitherto undetected products and intermediates in the C–H activation reaction of such iridium species, including a carboxaldehyde. The formation of the carboxaldehyde represents the first evidence that the cyclopentadienyliridium system can be photochemically activated to promote the carbonylation of alkanes.

Experimental Section

General: All operations were carried out using standard Schlenk techniques under an inert argon atmosphere unless otherwise stated. Cyclopentane (99+%), cyclohexane (99.9%), and hexane were distilled under nitrogen from sodium/benzophenone ketyl. Chlorotricarbonyliridium (Strem) was purchased and used without further purification.

NMR spectra were recorded with either a Bruker ACF 300 MHz or Bruker DPX 300 MHz spectrometer. Chemical shifts are reported with respect to residual solvent peaks. UV absorption spectra of starting complexes were recorded in cyclohexane with a Shimadzu 160 spectrometer. Gas chromatography (GC) analyses were performed with a HP 6890 gas chromatograph equipped with an HP 5973 mass-selective detector and a ZB-1 (30 m × 0.25 mm × 0.25 µm) capillary column, or with an HP5890 Series II plus equipped with an FID detector and a DB-5 (30 m × 0.32 mm × 0.25 µm) capillary column. Photolyses were carried out with either a Hanovia 450-W UV lamp with a nominal λ_{max} of 254 nm, or a continuum Surelite III 10-ns-pulse Nd-YAG laser operating at 3 mJ per pulse with 266-nm radiation.

IR spectra for routine analysis were recorded with a Bio-Rad FTS 165, a Digilab Excalibur Series FTS 3000MX, or a Shimadzu IR Prestige-21 FTIR-8400S FT-IR spectrometer at a resolution of 1 cm^{-1} using a solution IR cell with NaCl windows and a path length of 0.1 mm. IR spectra for in situ studies under ambient pressure were recorded with a Perkin–Elmer 2000 FTIR spectrometer at a resolution of 4 cm^{-1} using a high-pressure heatable liquid cell with ZnSe windows and a path length of 0.1 mm from Specac. IR spectra for high-pressure studies were taken in a thermostatted high-pressure cell constructed of 316 stainless steel and AMTIR windows with a path length of 0.5 mm; details of the design will be described elsewhere.[15] Only carbonyl stretches in the 1600–2200 cm^{-1} region are reported.

The compounds Cp^H,[16] Cp*^H,[17] $C_5H_5CH_2Ph$ ($Cp^{Bz}H$),[18] and $[Cp^*Ir(CO)_2]$ (**1b**)[19] were prepared following published procedures. Thallium salts were prepared following a literature method.[20] The complexes [Cp^Ir(CO)$_2$] (**1c**), [Cp*^Ir(CO)$_2$] (**1d**), and $[Cp^{Bz}Ir(CO)_2]$ (**1e**) were synthesized by a procedure analogous to that used for the synthesis of $[CpIr(CO)_2]$ (**1a**).[6]

Preparation of [Cp*^Ir(CO)$_2$]: Cp*^Li was prepared in situ from Cp*^H (98.2 mg, 0.509 mmol) and *n*BuLi (0.3 mL of a 2.2 M solution, 0.66 mmol) in hexane. The suspension was cannula transferred into a suspension of $[Ir(CO)_3Cl]$ (102 mg, 0.327 mmol) in hexane (10 mL) in a Carius tube. The mixture was degassed and heated at 70 °C for 2 d. The resultant mixture was cooled and filtered through celite to remove unreacted starting materials. The yellow filtrate was vacuum-dried to give **1d** as a yellow oil. IR (cyclohexane): $\tilde{\nu}$ = 1954, 2020 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 2.60–2.54 (m, 2 H, CH_2-N) 2.27 (s, 6 H, N-CH_3), 2.26–2.19 (m, 2 H, CH_2), 2.15 (s, 6 H, ring CH_3), 2.16 (s, 6 H, ring CH_3) ppm. The ^1H NMR spectroscopic data matched the literature values.[21,22]

Preparation of $[Cp^{Bz}Ir(CO)_2]$: A degassed suspension of $Cp^{Bz}Tl$ (55 mg, 0.154 mmol) and $[Ir(CO)_3Cl]$ (21.2 mg, 0.068 mmol) in hexane (20 mL) was heated in a Carius tube at 80 °C for 2 d. The resultant mixture was cooled and filtered through celite to remove unreacted starting materials. The yellow filtrate was vacuum-dried to give **1e** as a yellow oil. IR (cyclohexane): $\tilde{\nu}$ = 1969, 2036 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.23 (m, 5 H, C_6H_5), 5.45 (m, 2 H, C_5H_4), 5.37 (m, 2 H, C_5H_4), 3.77 (s, 2 H, CH_2) ppm. The IR data matched the literature values.[20]

Complex **1c** was prepared from Cp^Tl (432 mg, 1.265 mmol) and $[Ir(CO)_3Cl]$ (217 mg, 0.696 mmol) in an analogous manner. IR (cyclohexane): $\tilde{\nu}$ = 1967, 2034 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 5.52 (m, 2 H, C_5H_4), 5.37 (m, 2 H, C_5H_4), 2.58–2.36 (m, 4 H, CH_2CH_2), 2.26 (s, 6 H, N-CH_3) ppm. The ^1H NMR spectroscopic data matched the literature values.[20]

Preparative Photolysis: A solution of the metal complex in the hydrocarbon solvent (1 mg mL^{-1}) was placed in a closed quartz tube, degassed by three cycles of freeze-pump-thaw, and then irradiated with a 450-W water-cooled, medium-pressure mercury lamp placed approximately 15 cm away whilst being continuously stirred. For reaction under CO atmosphere, the quartz tube was refilled with 1 atm of CO from the Schlenk line after degassing. For the laser irradiation, dichroic mirrors were used to direct the pulses; cooling by water circulation was not necessary.

In situ IR Measurements: For measurements at ambient pressure, a well-stirred solution of **1b** or **1d** in cyclohexane was circulated between the quartz reactor and a ZnSe cell through Vitron (internal diameter 2.06 mm) and Tygon tubing using a peristaltic pump (MASTERflex C/L 5910 pump systems model 77120–62). UV irradiation was carried out through the quartz reactor. The reactor was fan-cooled and the temperature was not controlled. The atmosphere was either argon or carbon monoxide.

For the high-pressure measurements, a solution of **1b** in cyclohexane was circulated between a 100-mL stainless-steel autoclave type reactor, a high-pressure cell of original design (AMTIR windows), and an industrial sapphire tube (Almaz Optics, Inc., Marlton, New Jersey) of 5 mm internal diameter (I.D.) via stainless steel tubing of 1/16 inch i.d. under various CO pressures. UV irradiation was carried out through the sapphire tube. The temperature was kept at 20 °C by cryostatic control.

Acknowledgments

This work was supported by an A*STAR grant (research grant no. 012 101 0035), and K. I. K. and P. K. C. would like to thank the University for research scholarships.

---

[1] a) A. H. Janowicz, R. G. Bergman, *J. Am. Chem. Soc.* **1982**, *104*, 352–354; b) J. K. Hoyano, W. A. G. Graham, *J. Am. Chem. Soc.* **1982**, *104*, 3723–3725; c) A. H. Janowicz, R. A. Periana, J. M. Buchanan, C. A. Kovac, J. M. Stryker, M. J. Wax, R. G. Bergman, *Pure Appl. Chem.* **1984**, *56*, 13–23; d) S. T. Belt, F. W. Grevels, W. E. Klotzbucher, A. McCamley, R. N. Perutz, *J. Am. Chem. Soc.* **1989**, *111*, 8373–8382; e) A. A. Bengali, R. H. Schultz, C. B. Moore, R. G. Bergman, *J. Am. Chem. Soc.* **1994**, *116*, 9585–9589.

[2] a) J. M. Buchanan, J. M. Stryker, R. G. Bergman, *J. Am. Chem. Soc.* **1986**, *108*, 1537–1550; b) S. E. Bromberg, T. Lian, R. G. Bergman, C. B. Harris, *J. Am. Chem. Soc.* **1996**, *118*, 2069–2072; c) N. Dunwoody, S. Sun, A. J. Lees, *Inorg. Chem.* **2000**, *39*, 4442–4451.

[3] A. J. Lees, *J. Organomet. Chem.* **1998**, *554*, 1–11.

[4] C. Muller, D. Vos, P. Jutzi, *J. Organomet. Chem.* **2000**, *600*, 127–143.

[5] P. Jutzi, T. Redeker, *Eur. J. Inorg. Chem.* **1998**, 663–674.

[6] S. A. Gardner, P. S. Andrews, M. D. Rausch, *Inorg. Chem.* **1973**, *12*, 2396–2402.

[7] W. A. G. Graham, *J. Organomet. Chem.* **1986**, *300*, 81–91.

[8] D. M. Heinekey, D. A. Fine, T. G. P. Harper, S. T. Michel, *Can. J. Chem.* **1995**, *73*, 1116–1125.

[9] F. P. Pruchnik, K. Waijda-Hermanowicz, M. Koralewicz, *J. Organomet. Chem.* **1990**, *384*, 381–383.

[10] R. G. Bergman, *Science* **1984**, *223*, 902–908.

[11] a) W. Chew, E. Widjaja, M. Garland, *Organometallics* **2002**, *21*, 1982–1990; b) E. Widjaja, C. Li, M. Garland, *Organometallics* **2002**, *21*, 1991–1997.

[12] We observed no significant difference in product distribution for the experiments carried out at ambient pressure using Vitron tubing and those carried out under CO pressure using stainless-steel tubing.

[13] a) T. Sakakura, T. Sodeyama, K. Sasaki, K. Wada, M. Tanaka, *J. Am. Chem. Soc.* **1990**, *112*, 7221–7229; b) G. P. Rosini, K. M. Zhu, A. S. Goldman, *J. Organomet. Chem.* **1995**, *504*, 115–121; c) G. P. Rosini, W. T. Boese, A. S. Goldman, *J. Am. Chem. Soc.* **1994**, *116*, 9498–9505.

[14] M. Tanaka, T. Sakukara, in *Homogeneous Transition Metal Catalyzed Reactions* (Eds.: W. R. Moser, D. W. Slocum); Advances in Chemistry Series 230; American Chemical Society: Washington, DC, **1992**, chapter 12, pp 181–196.

[15] F. Gao, K. P. Ng, C. Li, K. I. Krummel, A. D. Allian, M. A. Garland, *J. Catal*. **2006**, *237*, 49–57.

[16] T. F. Wang, T. Y. Lee, *J. Organomet. Chem.* **1992**, *423*, 31–38.

[17] P. Jutzi, J. Dahlhaus, *Synthesis* **1993**, *7*, 684–686.

[18] P. Singh, M. D. Rausch, *J. Organomet. Chem.* **1988**, *352*, 273–282.

[19] R. G. Ball, W. A. G. Graham, D. M. Heinekey, J. K. Hoyano, A. D. McMaster, B. M. Mattson, S. T. Michel, *Inorg. Chem.* **1990**, *29*, 2023–2025.

[20] M. S. Blais, J. C. W. Chien, M. D. Raush, *Organometallics* **1998**, *17*, 3775–3783.

[21] M. S. Blais, M. D. Rausch, *J. Organomet. Chem.* **1995**, *502*, 1–8.

[22] P. Jutzi, M. O. Kristen, B. Neumann, H. G. Stammler, *Organometallics* **1994**, *13*, 3854–3861.

Received: November 24, 2005