Inorg. Chem. **1994**, *33*, 3021–3022

Synthesis of Metal Fullerene Derivatives from Chloro Hydrido Transition Metal Complexes

Serge Schreiner,*[1a] Thomas N. Gallaher,[1b] and Henri K. Parsons[1c]

Departments of Chemistry, Randolph-Macon College,
Ashland, Virginia 23005,
and James Madison University,
Harrisonburg, Virginia 22807

Received September 23, 1993

Introduction

Following the discovery that C$_{60}$[2] can be prepared in relatively large quantities,[3] a number of studies have been undertaken to investigate the chemical reactivity of this molecule. Some of these efforts have been directed toward its reactions with low-valent transition metal complexes.[4] In this note, we wish to report the synthesis of C$_{60}$–metal complexes by elimination of HCl from chloro hydrido platinum and iridium complexes followed by addition of C$_{60}$ to a coordinatively unsaturated, reactive intermediate.

Reductive elimination of HCl from chloro hydrido transition metal complexes under homogeneous conditions has been successfully employed for a number of compounds in the synthesis of organometallic complexes.[5] These reactions are either effected in one step or two step processes. In particular, [Pt(H)(Cl)(PPh$_3$)$_2$],[6] **1**, and [Ir(H)$_2$(Cl)(CO)(PPh$_3$)$_2$],[7] **2**, have been reported to react in the presence of a base and PPh$_3$ to yield [Pt(PPh$_3$)$_3$],[8] **3**, and [Ir(H)(CO)(PPh$_3$)$_3$],[9] **4**, respectively. These observations lead us to investigate the reactions of these complexes with C$_{60}$ as a possible general synthetic route for the preparation of transition metal–C$_{60}$ complexes.

Results and Discussion

Reaction of the 16-electron, square-planar complex [Pt(H)(Cl)(PPh$_3$)$_2$], **1**, with C$_{60}$ in refluxing ethanol/benzene (1:2) in the presence of ethanolic NaOH resulted in the formation of a dark green solid which is soluble in benzene and THF. Elemental analysis of this complex is consistant with its formulation as [Pt(η^2-C$_{60}$)(PPh$_3$)$_2$], **5**. The ^{31}P{^{1}H} spectrum of **5** shows a triplet at 27.3 ppm ($^1J_{\text{Pt-P}}$ = 3929 Hz) which is 1.9 ppm lower than that for **1** (t, 29.2 ppm, $^1J_{\text{Pt-P}}$ = 3023 Hz). The platinum resonance in the ^{195}Pt{^{1}H} NMR spectrum of **2** (t, –4925 ppm) is shifted 109 ppm more negative than the chloro hydrido complex (t, –4816 ppm) while the hydride ligand resonance which is found at –15.2 ppm ($^1J_{\text{Pt-H}}$ = 582.1 Hz) in the ^{1}H NMR for the starting complex is not present in the spectrum of the product complex. Identical spectroscopic data for the product were obtained when using [Pt(H)(Br)(PPh$_3$)$_2$] as the starting complex. These data are consistant with that for the previously reported preparation of **5** by reaction of [Pt(η^2-C$_2$H$_4$)(PPh$_3$)$_2$] with C$_{60}$ in THF.[4f]

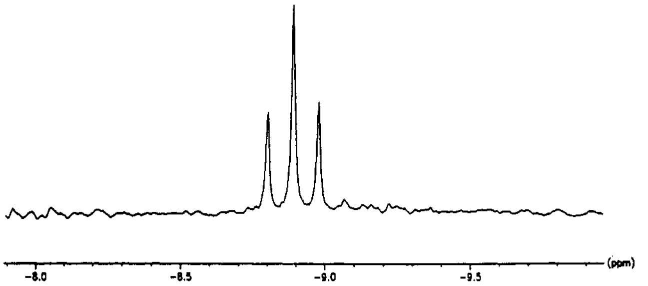

Figure 1. ^{1}H NMR spectrum of the hydride region of [Ir(H)(CO)(η^2-C$_{60}$)(PPh$_3$)$_2$].

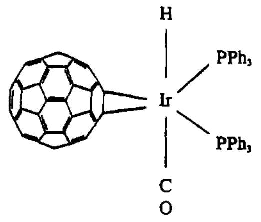

Figure 2. Proposed structure of [Ir(H)(CO)(η^2-C$_{60}$)(PPh$_3$)$_2$].

Reaction of the 18-electron, octahedral complex [Ir(H)$_2$(Cl)(CO)(PPh$_3$)$_2$], **2**, with C$_{60}$ under the same reaction conditions yields a novel, green compound formulated as [Ir(H)(CO)(η^2-C$_{60}$)(PPh$_3$)$_2$], **6**. ^{31}P{^{1}H} spectra show a shift of the singlet from 11.1 ppm for **2** to 8.3 ppm for **6**. The ^{1}H NMR spectrum of **6** is characterized by a hydride resonance at –9.02 ppm (t, 1:2:1) with a $^2J_{\text{P-H}}$ = 17.3 Hz which is typical for a hydride cis to two equivalent phosphorus atoms[10] (Figure 1). This is in contrast to the starting complex, **2**, which exhibits two hydride resonnances at –7.4 ppm (dt, $^2J_{\text{P-H}}$ = 9.4 Hz) and at –18.5 ppm (dt, $^2J_{\text{P-H}}$ = 12.9 Hz). The ^{13}C{^{1}H} NMR spectrum of **6** exhibits a carbon resonance at 180.7 (t) with a $^2J_{\text{P-C}}$ = 5.2 Hz characteristic of the carbonyl carbon as well as multiple resonances attributed to coordinated C$_{60}$.[4c] The infrared spectrum of **6** (KBr) shows two significant absorptions at 1985 cm^{-1} (υ_{CO}) and at 2102 cm^{-1} ($\upsilon_{\text{Ir-H}}$) while complex **2** is characterized by a CO stretching vibration at 1979 cm^{-1} and two metal–hydride stretching vibrations at 2106 and 2193 cm^{-1}. The proposed structure of **6** is shown in Figure 2. Coordination of iridium is believed to occur at the fusion of two six-membered rings since these bonds are shorter and exhibit the most double bond character. This is in agreement with all previously reported C$_{60}$–metal complexes. In particular, the proposed structure appears to be similar to the structure of the recently reported isoelectronic rhodium complex, [Rh(H)(CO)(η^2-C$_{60}$)(PPh$_3$)$_2$].[4l] Attempts to isolate the presumed intermediate [Ir(H)(CO)(PPh$_3$)$_2$], **7**, were not successful. This observation is consistant with the earlier reported instability of **7** under similar reaction conditions and its disproportionation to [Ir(H)(CO)(PPh$_3$)$_3$], **4**, and other reaction products.[9] It is noteworthy to report that complex **6** can also be obtained by direct reaction of

---

(1) (a) Randolph-Macon College. (b) James Madison University. (c) NSF REU student from Hampton University at James Madison University.

(2) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162.

(3) Krätschmer, W.; Lamb, L. D.; Fostiropoulis, K; Huffman, D. R. *Nature* **1990**, *347*, 354.

(4) (a) Hawkins, J. M.; Lewis, T. A.; Loren, S. D; Meyer, A.; Heath, J. R.; Shibata, Y.; Saykally, R. J. *J. Org. Chem.* **1990**, *55*, 6250. (b) Hawkins, J. M.; Meyer, A.; Lewis, T. A.; Loren, S.; Hollander, F. J. *Science* **1991**, *252*, 312. (c) Hawkins, J. M.; Loren, S. D.; Meyer, A; Nunlist, R. *J. Am. Chem. Soc.* **1991**, *113*, 7770. (d) Hawkins, J. M. *Acc. Chem. Res.* **1992**, *25*, 150. (e) Fagan, P. J.; Calabrese, J. C.; Malone, B. *Science* **1991**, *252*, 1160. (f) Fagan, P. J.; Calabrese, J. C.; Malone, B. *J. Am. Chem. Soc.* **1991**, *113*, 9408. (g) Fagan, P. J.; Calabrese, J. C.; Malone, B. *Acc. Chem. Res.* **1992**, *25*, 134. (h) Koefed, R. S.; Hudgens, M. F.; Shapley, J. R. *J. Am. Chem. Soc.* **1991**, *113*, 8957. (i) Balch, A. L.; Catalano, V. J.; Lee, J. W. *Inorg. Chem.* **1991**, *30*, 3980. (j) Balch, A. L.; Catalano, V. J.; Lee, J. W.; Olmstead, M. M. *J. Am. Chem. Soc.* **1992**, *114*, 5455. (k) Bashilov, V. V.; Petrovskii, P. V.; Sokolov, V. I.; Lindeman, S. V.; Guzey, I. A.; Struchkov, Y. T. *Organometallics* **1993**, *12*, 991. (l) Balch, A. L.; Lee, J. W.; Noll, B. C.; Olmstead, M. M. *Inorg. Chem.* **1993**, *32*, 3577. (m) Zhang, S.; Brown, T. L.; Du, Y.; Shapley, J. R. *J. Am. Chem. Soc.* **1993**, *115*, 6705.

(5) Grushin, V. V. *Acc. Chem. Res.* **1993**, *26*, 279.

(6) Bailar, J. C.; Itatani, H. *Inorg. Chem.* **1965**, *4*, 1618.

(7) Vaska, L.; DiLuzio, J. W. *J. Am. Chem. Soc.* **1962**, *84*, 679.

(8) Cariati, F.; Ugo, R.; Bonati, F. *Inorg. Chem.* **1966**, *5*, 1128.

(9) Harrod, J. F.; Gilson, D. F. R.; Charles, R. *Can. J. Chem.* **1969**, *47*, 1431.

(10) Crabtree, R. H.; Felkin, H.; Fillebeen-Khan, T.; Morris, G. E. *J. Organomet. Chem.* **1979**, *168*, 183.

0020-1669/94/1333-3021$04.50/0

[Ir(H)(CO)(PPh$_3$)$_3$],[11] **4**, with C_{60} in benzene followed by precipitation with hexanes.[12]

Further investigations of C_{60} reactivity toward metal fragments generated from other chloro hydrido transition metal complexes are in progress.

Experimental Section

Under an atmosphere of dinitrogen, 50.6 mg (0.061 mmol) of **1** and 48.0 mg (0.061 mmol) of C_{60} were added to a solution of ethanol (20 mL), benzene (40 mL), and sodium hydroxide (1 mL, 0.89 M in ethanol). The solution mixture was refluxed for 2 h during which time the color of the solution changed to dark green. The reaction mixture was allowed to cool to room temperature and a green-black solid was collected by filtration after precipitation with hexanes (50 mL) and washing with 10 mL of ethanol. Recrystallization from THF/hexanes yielded a green-black solid. Yield, analysis, and spectroscopic data for **5** were as follows. Yield: 79.8 mg (84%). Anal. Calcd for $C_{96}H_{30}P_2Pt$: C, 80.0; H, 2.08. Found: C, 81.3; H, 2.13. ^{1}H NMR (200 MHz, THF-*d*$_8$): δ 6.8–7.8 (m, C_6H_5). $^{31}P\{^1H\}$ NMR (81.015 MHz, THF-*d*$_8$): δ 27.3 (t, $^1J_{Pt-P}$ = 3929 Hz). $^{195}Pt\{^1H\}$ NMR (43.02 MHz, THF-*d*$_8$): δ −4925 (t, $^1J_{Pt-P}$ = 3924 Hz).

Complex **6** was prepared analogously as described for **5** from **2**. Reaction of 50.0 mg, (0.064 mmol) of [Ir(H)$_2$(Cl)(CO)(PPh$_3$)$_2$] with 46.2 mg of C_{60} (0.064 mmol) produced a dark green solid. Yield, analysis, and spectroscopic data for **6** were as follows. Yield: 40.4 mg, (43%). Anal. Calcd for $C_{97}H_{46}IrOP_2$: C, 79.4; H, 2.12. Found: C, 79.9; H, 2.39. IR (KBr): 2102 cm^{-1} (ν_{Ir-H}); 1985 cm^{-1} (ν_{CO}). ^{1}H NMR (200 MHz, THF-*d*$_8$): δ 6.8–7.7 (m, C_6H_5); δ −9.02 (t, H, $^2J_{P-H}$ = 17.3 Hz). $^{13}C\{H\}$ NMR (50.333 MHz, THF-*d*$_8$): δ 180.7 (t, carbonyl carbon, $^2J_{P-C}$ = 5.2 Hz). $^{31}P\{^1H\}$ NMR (81.015 MHz, THF-*d*$_8$): δ 8.3 (s).

Complex **6** was also prepared from compound **4**: under an atmosphere of dinitrogen, 50.4 mg (0.500 mmol) of **4** and 36.0 mg (0.500 mmol) of C_{60} were added to benzene (10 mL). Within 30 min the solution became dark green. Precipitation with hexanes (50 mL) yielded a dark green solid which was recrystallized from THF/hexanes. Yield: 57.1 mg (78%).

Acknowledgment. This work was supported in part by the Walter Williams Craigie Teaching Endowment administered through Randolph-Macon College and the National Science Foundation (Grant CHE-900261).

---

(11) Bath, S. S; Vaska, L. *J. Am. Chem. Soc.* **1963**, *85*, 3500.

(12) Balch and co-workers reported the preparation of [Rh(H)(CO)(η^2-C_{60})(PPh$_3$)$_2$] by a similar procedure.[4l]