DOI: 10.1002/ejic.200700814

The First Example of a Bis(trifluoromethyl)carbene Transition-Metal Complex and Its Reduction to a Perfluoroallene Complex

Jian Yuan,[a] Russell P. Hughes,*[a] and Arnold L. Rheingold[b]

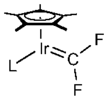
Dedicated to Dr. Robert M. Ross on the occasion of his 90th birthday

Keywords: Carbene / Iridium / Fluorine / Ligands / Structure

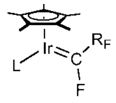
Na/Pb alloy reduction of the (perfluoroisopropyl)iridium complex Cp*(CO)IrI[CF(CF$_3$)$_2$] afforded the first example of a bis(trifluoromethyl)carbene complex, Cp*(CO)Ir=C(CF$_3$)$_2$, which has been crystallographically characterized. Further reduction of this carbene complex with KC$_8$ yielded the perfluoroallene iridium complex Cp*Ir(CO)(η^2-CF$_2$CCF$_2$).

Introduction

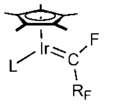
Transition-metal complexes with carbene ligands have been known for more than four decades,[1,2] and they have been extensively utilized in organic synthesis and catalysis.[3,4] Other than compounds of the parent methylene ligand,[5] all such complexes isolated to date contain at least one carbene substituent (alkyl, aryl, heteroatom) that is electron-donating in a σ- or π-sense. Recently we reported a simple reductive conversion of primary (perfluoroalkyl)iridium complexes to difluorocarbene complexes **1** and **2**. The (difluorocarbene)iridium complexes are stable, crystalline solids, unlike the CH$_2$ analogue of **1**, which can only be observed spectroscopically at low temperatures,[6] even though other terminal methylene complexes of iridium are stable enough for isolation.[7,8] Similarly, fluoro(perfluoroalkyl)carbene complexes **3**–**6** can be isolated by using sodium naphthalenide (NaNp), potassium graphite (KC$_8$), or magnesium graphite [C$_{16}$Mg(KCl)$_2$] as electron sources.[9,10] While compounds **3**–**6** contain one perfluoroalkyl substituent, which is an exclusively electron-withdrawing group,[11–14] the other fluorine substituent at the carbene carbon is still capable of π-donation. Here we report the first example of a complex with a carbene ligand bearing two electron-withdrawing trifluoromethyl substituents, which can be isolated as a stable, sublimable solid.



1 L = PMe$_3$
2 L = CO



3a–6a



3b–6b

3a,b L = PMe$_3$, R$_F$ = CF$_3$
4a,b L = CO, R$_F$ = CF$_3$
5a,b L = PMe$_3$, R$_F$ = CF$_2$CF$_3$
6a,b L = CO, R$_F$ = CF$_2$CF$_3$

Results and Discussion

Careful two-electron reduction of perfluoroisopropyl complex **7**[15] in thf by using Na/Pb alloy (Na ca.10%) afforded bis(trifluoromethyl)carbene complex **8** in 87% yield as a yellow, crystalline, sublimable, air-stable compound, unambiguously characterized by a single-crystal X-ray diffraction study. An ORTEP is shown in Figure 1 (Figure 1). The Ir–C double bond length of 1.928(7) Å is significantly shorter than the Ir–C single bond in **7** [2.11(3) Å][15] and slightly longer than the double bond in its difluorocarbene analogue **2** [1.855(13) Å].[10] Not unexpectedly, the CF$_3$–Ir–CF$_3$ angle in **8** [110.0(6)°] is substantially larger than the F–C–F angle in **2** [103.5(10)°].[10]

Complex **8** represents the first unambiguously characterized compound of a carbene ligand bearing two perfluoroalkyl groups; an early attempt by others to prepare such a compound by reaction of *trans*-(Ph$_2$MeP)$_2$Ir(CO)Cl with the diazo precursor (CF$_3$)CN$_2$ gave a poorly characterized product in which it was not possible to distinguish between structure **9a** or **9b** (L = PMePh$_2$).[16] Notably, a terminal methylene analogue of **9b** can be isolated in a similar reaction by using diazomethane.[7]

While the mono(perfluoroalkyl)carbene analogues **3**–**6** are inert to further reduction, the new bis(trifluoromethyl)-

---

[a] Department of Chemistry, Dartmouth College, 6128 Burke Laboratories
Hanover, NH 03755, USA
Fax: +1-603-646-3946
E-mail: rph@dartmouth.edu
[b] Department of Chemistry, University of California, San Diego
San Diego, CA 92093, USA

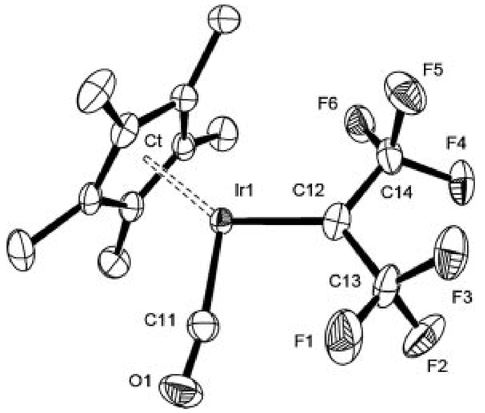


Figure 1. ORTEP diagram of the non-hydrogen atoms of **8**, showing the partial atom-labeling scheme. Thermal ellipsoids are shown at the 30% level. Selected bond lengths [Å] and angles [°]: Ir1–C11 1.860(7), Ir1–C12 1.928(7), Ir1–Ct 1.889(6), C12–C14 1.481(11), C12–C13 1.489(10), O1–C11 1.129(8); Ct–Ir1–C12 140.5(3), Ct–Ir1–C11 124.9(3), C11–Ir1–C12 94.7(3), C14–C12–C13 110.0(6), C14–C12–Ir1 123.6(5), C13–C12–Ir1 126.4(6).

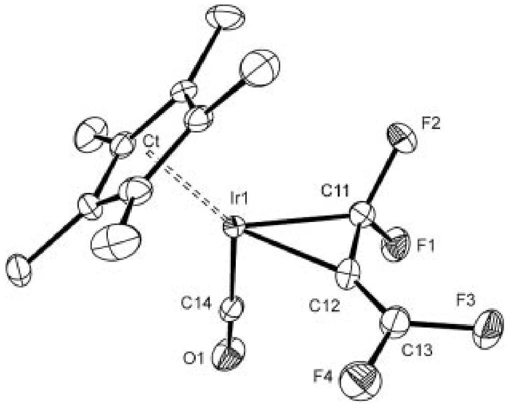
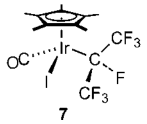
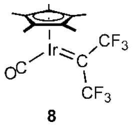


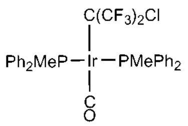
Figure 2. ORTEP diagram of the non-hydrogen atoms of **10** showing the partial atom-labeling scheme. Thermal ellipsoids are shown at the 30% level. Selected bond lengths [Å] and angles [°]: Ir1–C11 2.035(7), C11–F1 1.381(8), C11–F2 1.362(8), Ir1–C12 2.030(7), C11–C12 1.426(10), C12–C13 1.281(10), C13–F3 1.337(8), C13–F4 1.340(9), Ir1–C14 1.862(6), C14–O1 1.133(7); Ir1–C11–C12 69.3(4), Ir1–C12–C11 69.6(4), C12–Ir1–C11 41.1(3), C11–C12–C13 138.8(7), C13–C12–Ir1 151.3(6).



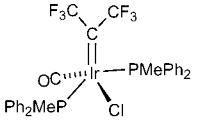
7



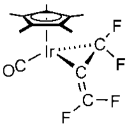
8



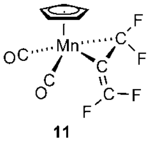
9a



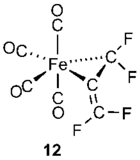
9b



10



11



12

carbene complex **8** is more reactive, undergoing reduction by KC_8 to eliminate two more fluorides and afford (perfluoroallene)iridium complex **10** in 60% yield as a white crystalline compound. It was also possible to synthesize **10** from the direct reduction of **7** with excess KC_8. The structure is also unambiguously defined by means of a single-crystal X-ray diffraction study; an ORTEP representation of the structure is shown in Figure 2. As expected, the allene ligand is bent with a C–C–C angle of 138.8(7)°, and the coordinated alkene [1.426(10) Å] is longer than the uncoordinated one [1.281(10) Å]. This is only the third example of a structurally characterized perfluoroallene complex and differs from its first-row metal analogues **11**[17] and **12**[18] in that the two Ir–C distances [2.035(7) Å and 2.030(7) Å] are equal within experimental error. In compounds **11** and **12**, the distance of the metal to the internal allene carbon is significantly shorter than that to the terminal carbon. Observation of four well-resolved doublet of doublet of doublet signals in the solution ^{19}F NMR spectrum indicate that there is a high barrier to propeller rotation of the allene ligand in **10**; propeller rotation on the NMR timescale would interconvert the resonances of F1 and F2. All four resonances were unambiguously assigned by means of a $^{19}F\{^1H\}$ HOESY experiment.

Conclusions

This methodology illustrates that the presence of donor substituents other than H is not a requirement for stability in transition-metal carbene complexes. In addition, it demonstrates that reductive inner-sphere construction of unsaturated fluorocarbon ligands like tetrafluoroallene and the previously reported example of tetrafluorobutatriene[19] represent useful alternative methods for their synthesis as opposed to the direct ligand substitution required when starting with the free fluorocarbon,[18,20,21] which itself can be difficult to prepare and handle. Further experimental and computational studies of the structures and reactivity of this new class of carbene complexes will be reported in due course.

Experimental Section

Complex 8: To a Schlenk flask containing Na/Pb alloy (353 mg, 10 equiv.) and thf (6 mL) was added $Cp^*Ir(CO)(I)[CF(CF_3)_2]$ (100 mg, 0.154 mmol) as a solid, and the mixture was stirred at room temperature for 3 h. The solvent was removed, and the product was extracted into hexanes. Removal of solvent gave a yellow solid (68 mg, 87%). Crystals were obtained by sublimation (5 Torr, 70 °C). $C_{14}H_{15}F_6IrO$ (505.46): calcd. C 33.27, H 3.00; found C 33.19, H 3.45. IR (hexanes): ν(CO) = 2017 cm^{-1}. ^1H NMR (500 MHz, C_6D_6, 21 °C): $\delta = 1.51$ (s, C_5Me_5) ppm. ^{19}F NMR (470.31 MHz, C_6D_6, 21 °C): $\delta = -54.5$ (q, $^5J_{FF} = 8$ Hz, 3 F, CF_3), –57.1 (q, $^5J_{FF} = 8$ Hz, 3 F, CF_3) ppm. $^{13}C\{^1H\}$ NMR (125.7 Hz, C_6D_6, 21 °C): $\delta = 9.5$ (q, $^5J_{CF} = 1.2$ Hz, $C_5\mathit{Me}_5$), 100.7 (s, C_5Me_5), 134.6 (qq, $^1J_{CF}$ = 275, $^3J_{CF}$ = 5 Hz, CF_3), 137.0 (qq, $^1J_{CF}$ = 275, $^3J_{CF}$ = 6 Hz, CF_3), 177.9 (qq, $^4J_{CF}$ = 5, $^3J_{CF}$ = 1 Hz, CO), 182.1 (qq, $^2J_{CF}$ = $^2J_{CF}$ = 32 Hz, IrC) ppm. Crystal data for **8**: $C_{14}H_{15}F_6IrO$, M_r = 505.46, triclinic, space group $P\bar{1}$, V = 783.8(4) Å^3, a = 8.457(2) Å, b = 8.686(3) Å, c = 11.577(3) Å, α = 85.951(5)°, β = 76.850(6)°, γ = 71.198(5)°, Z = 2, T = 208(2) K, Mo-K_α = 0.71073 Å. GOF = 1.079. The final $R1(F^2)$ was 0.0343 for 3450 reflections $I > 2\sigma(I)$.

Complex 10: *Method A:* To a Schlenk flask containing KC_8 (183 mg, 1.35 mmol, 10 equiv.) and thf (6 mL) was added a solution of **8** (68 mg, 0.135 mmol) in thf (2 mL). The suspension was stirred at room temperature for 2 h. The solvent was removed, and the product was extracted into hexanes. Removal of solvent gave an off-white solid, (38 mg, 60%). *Method B:* To a Schlenk flask containing KC_8 (311.5 mg, 2.30 mmol, 10 equiv.) and thf (6 mL) was added. Cp*Ir(CO)(I)[CF(CF_3)$_2$] (150 mg, 0.230 mmol) as a solid. The suspension was stirred at room temperature for 2 h. The solvent was removed, and the product was extracted into hexanes. Removal of solvent gave an off-white solid (65 mg, 61%). Crystals were obtained from diffusion of neopentane into an ethyl isopropyl ether solution. $C_{14}H_{15}F_4IrO$ (467.49): calcd. C 35.97, H 3.23; found C 36.07, H 3.15. IR(hexane): ν(CO) = 2017 cm^{-1}, ν(C=CF_2) = 1787 cm^{-1}. ^{1}H NMR (500 MHz, C_6D_6, 21 °C): δ = 1.56 (s, C_5Me_5) ppm. ^{19}F NMR (470.31 MHz, C_6D_6, 21 °C): δ = –55.3 (ddd, $^2J_{FF}$ = 61, $^4J_{FF}$ = 9, $^4J_{FF}$ = 8 Hz 1 F, CF_2), F3; –84.7 (ddd, $^2J_{FF}$ = 133, $^4J_{FF}$ = 9, $^4J_{FF}$ = 9 Hz, 1 F, IrCF_2), F1; –93.8 (ddd, $^2J_{FF}$ = 61, $^4J_{FF}$ = 9, $^4J_{FF}$ = 9 Hz, 1 F, CF_2), F4; –101.1 (ddd, $^2J_{FF}$ = 133, $^4J_{FF}$ = 9, $^4J_{FF}$ = 8 Hz, 1 F, IrCF_2), F2 ppm. ^{13}C{^{1}H} NMR (125.7 Hz, C_6D_6, 21 °C): δ = 9.1 (s, C_5*Me*$_5$), 45.0 (dddd, $^2J_{CF}$ = 51, $^2J_{CF}$ = 12, $^2J_{CF}$ = 7, $^2J_{CF}$ = 5 Hz, IrC), 99.1 (s, *C*$_5$Me$_5$), 97.4 (tdd, $^1J_{CF}$ = 316, $^3J_{CF}$ = 21, $^3J_{CF}$ = 2 Hz, C=CF_2), 148.5 (ddt, $^1J_{CF}$ = 294, $^1J_{CF}$ = 274, $^3J_{CF}$ = 2 Hz, IrCF_2), 169.7 (dd, $^3J_{CF}$ = 11, $^3J_{CF}$ = 2 Hz, CO) ppm. Crystal data for **10**: $C_{14}H_{15}F_4IrO$, M_r = 467.46, orthorhombic, space group *Pbca*, V = 2949.4(5) Å^3, a = 14.3156(13) Å, b = 13.9844(13) Å, c = 14.7327(13) Å, $\alpha = \beta = \gamma$ = 90°, dummy 90°, 90 °C, 90 °C, (2)°, (2)° dummy Z = 8, T = 208(2) K, Mo-K_α = 0.71073 Å. GOF = 1.040. The final $R1(F^2)$ was 0.0482 for 3554 reflections $I > 2\sigma(I)$.

CCDC-655232 (**8**) and CCDC-655233 (**10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic data Centre via http://www.ccdc.uk/data_request/cif.

Acknowledgments

This work was supported by the U. S. National Science Foundation and the Petroleum Research Fund administered by the American Chemical Society.

---

[1] E. O. Fischer, A. Maasböl, *Angew. Chem.* **1964**, *76*, 645; *Angew. Chem. Int. Ed. Engl.* **1964**, *3*, 580–581.
[2] R. R. Schrock, *J. Am. Chem. Soc.* **1974**, *96*, 6796–6797.
[3] R. R. Schrock, *Angew. Chem. Int. Ed.* **2006**, *45*, 3748–3759.
[4] R. H. Grubbs, *Angew. Chem. Int. Ed.* **2006**, *45*, 3760–3765.
[5] R. R. Schrock, *J. Am. Chem. Soc.* **1975**, *97*, 6577–6578.
[6] D. P. Klein, R. G. Bergman, *J. Am. Chem. Soc.* **1989**, *111*, 3079–3080.
[7] G. R. Clark, W. R. Roper, A. H. Wright, *J. Organomet. Chem.* **1984**, *273*, C17–C19.
[8] M. D. Fryzuk, X. Gao, K. Joshi, P. A. MacNeil, R. L. Massey, *J. Am. Chem. Soc.* **1993**, *115*, 10581–10590.
[9] R. P. Hughes, R. B. Laritchev, J. Yuan, J. A. Golen, A. N. Rucker, A. L. Rheingold, *J. Am. Chem. Soc.* **2005**, *127*, 15020–15021.
[10] C. J. Bourgeois, R. P. Hughes, J. Yuan, A. G. DiPasquale, A. L. Rheingold, *Organometallics* **2006**, *25*, 2908–2910.
[11] B. E. Smart in *Chemistry of Functional Groups*, supplement D, vol. 1, chapter 14 (Eds.: S. Patai, Z. Rappoport), Wiley, New York, **1983**, pp. 603–655.
[12] B. E. Smart, *Mol. Struct. Eng.* **1986**, *3*, 141–191.
[13] R. E. Banks, B. E. Smart, J. C. Tatlow (Eds.), *Organofluorine Chemistry: Principles and Commercial Applications*, Plenum Press, New York, **1994**, pp. 644.
[14] B. E. Smart, *J. Fluorine Chem.* **2001**, *109*, 3–11.
[15] R. P. Hughes, J. M. Smith, L. M. Liable-Sands, T. E. Concolino, K.-C. Lam, C. Incarvito, A. L. Rheingold, *J. Chem. Soc. Dalton Trans.* **2000**, 873–879.
[16] J. Cooke, W. R. Cullen, M. Green, F. G. A. Stone, *Chem. Commun. (London)* **1968**, 170–171.
[17] D. Lentz, S. Willemsen, *Organometallics* **1999**, *18*, 3962–3964.
[18] D. Lentz, N. Nickelt, S. Willemsen, *Chem. Eur. J.* **2002**, *8*, 1205–1217.
[19] R. P. Hughes, R. B. Laritchev, L. N. Zakharov, A. L. Rheingold, *J. Am. Chem. Soc.* **2004**, *126*, 2308–2309.
[20] F. A. Akkerman, D. Lentz, *Angew. Chem. Int. Ed.* **2007**, *46*, 4902–4904.
[21] D. Lentz, *J. Fluorine Chem.* **2004**, *125*, 853–861.

Received: August 2, 2007