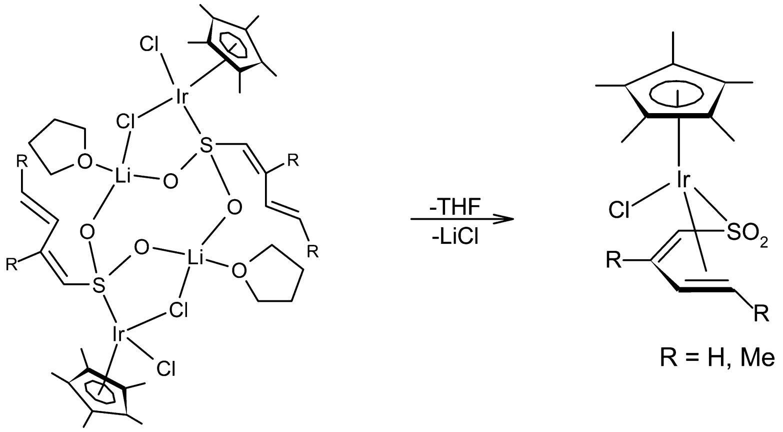
ORGANOMETALLICS

Article

Synthesis, NMR, and X-ray Molecular Structure of a Butadienesulfinate Iridium Dimer and Its Transformation into a Mononuclear Cp*IrCl[(1,2,5-)-SOCHCRCHCHR] Complex

Prcoro Gamero-Melo, Marisol Cervantes-Vsquez, Armando Ramirez-Monroy, M. Esther Snchez-Castro, and M. Angeles Paz-Sandoval

Organometallics, **2004**, 23 (13), 3290-3295 • DOI: 10.1021/om040021s



Organometallics is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

3290 *Organometallics* **2004,** *23,* 3290−3295

Synthesis, NMR, and X-ray Molecular Structure of a Butadienesulfinate Iridium Dimer and Its Transformation into a Mononuclear Cp*IrCl[(1,2,5-η)-$SO_2CH{=}CRCH{=}CHR$] Complex

Prócoro Gamero-Melo, Marisol Cervantes-Vásquez, Armando Ramirez-Monroy,
M. Esther Sánchez-Castro, and M. Angeles Paz-Sandoval*

Departamento de Quimica, Centro de Investigación y de Estudios Avanzados del IPN,
Apartado Postal 14-740, Mexico 07000, D.F., Mexico, and Av. IPN # 2508,
San Pedro Zacatenco, Mexico 07360, D.F., Mexico

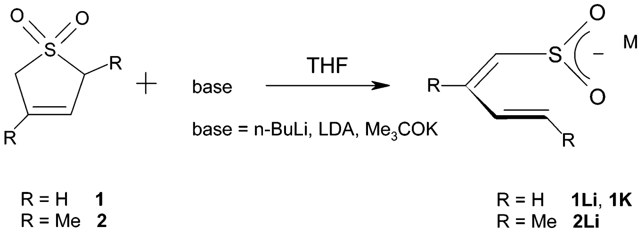
Received February 25, 2004

A metathesis reaction of $[Cp^*IrCl_2]_2$ with butadienesulfinate lithium ($SO_2CHCRCHCHR$)-Li (R = H, **1Li**; Me, **2Li**) affords the dinuclear compounds $[Cp^*Ir(Cl)_2\{(5\text{-}\eta)\text{-}SO_2CH{=}CRCH{=}CHR\}(Li)(THF)]_2$ (R = H, **3**; Me, **4**), respectively. The single-crystal X-ray analysis of **3** and **4** reveals the presence of metallacyclic, five- and eight-membered rings, which easily break to afford compounds Cp*IrCl[(1,2,5-η)-$SO_2CH{=}CRCH{=}CHR$] [R = H, (**5**), Me (**6**)], upon displacement of THF and LiCl. The ^1H and ^{13}C NMR data are consistent with the single-crystal X-ray diffraction structures of **3** and **4**. Compounds **5** and **6** showed that the butadienesulfonyl ligands are coordinated through the sulfur atoms and the terminal double bonds, according to the X-ray study of compound **5** and NMR spectroscopy. Immediate formation of compound **5** can be achieved in 83% yield from $[Cp^*IrCl_2]_2$ and **1K**, showing that the alkaline metal is crucial in the isolation of the lithium derivatives **3** and **4**.

Introduction

Few reports have been published on the corresponding oxidative derivatives of the thiapentadienyl[1−4] anion $(SCHCHCHCH_2)^-$, such as the sulfinylpentadienyl[5] $(OSCHCHCHCH_2)^-$ and the butadienesulfinate[1,5−7] $(CH_2{=}CHCH{=}CHSO_2)^-$ anions, and consequently, their development as ligands in organometallic compounds is not known. The lack of well-defined and easy methodologies to prepare dienesulfinates and sulfinylpentadienyl salts promoted our interest in the investigation of the deprotonation reaction of the 2,5-dihydrothiophene-1-oxide and 2,5-dihydrothiophene-1,1-dioxide (**1**) and some methyl-substituted analogues, with different bases.[8] The reactions of **1** and 2,4-dimethyl-2,5-dihydrothiophene-1,1-dioxide (**2**) with bases, such as *n*-BuLi, LDA (lithium diisopropylamide), and *t*-BuOK, give the corresponding salts $(CH_2{=}CHCH{=}CHSO_2)Li$ (**1Li**), $(MeCH{=}CHC(Me){=}CHSO_2)Li$ (**2Li**), and $(CH_2{=}CHCH{=}CHSO_2)K$ (**1K**), respectively, Scheme 1. The study of these compounds allowed the clarification of structural aspects and improvement their synthetic methods.[8] This paper describes the reactivity of these salts toward $[Cp^*IrCl_2]_2$ in a typical metathesis reaction.

Scheme 1



Results and Discussion

Treatment of $[Cp^*IrCl_2]_2$ with butadienesulfinate lithium ($SO_2CHCRCHCHR$)Li (R = H, **1Li**; Me, **2Li**) (Scheme 1) produces $[Cp^*Ir(Cl)_2\{(5\text{-}\eta)\text{-}SO_2CH{=}CRCH{=}CHR\}(Li)(THF)]_2$ (R = H, **3**; Me, **4**) in ca. 17 and 45% yield, respectively (Scheme 2).

Compounds **3** and **4** precipitated from THF/diethyl ether, giving orange-yellow crystals along with a yellow powder of Cp*IrCl[(1,2,5-η)-$SO_2CH{=}CRCH{=}CHR$] [R = H, (**5**), Me (**6**)].[9] As soon as compounds **3** and **4** are in chloroform, they are transformed to the corresponding yellow compounds **5** and **6** upon displacement of the THF and LiCl, Scheme 2.

---

* To whom correspondence should be addressed. Tel: (52) 55 50613717. E-mail: mpaz@mail.cinvestav.mx.

[1] Kloosterziel, H.; van Drunen, J. A. A.; Galama, P. *J. Chem. Soc., Chem. Comm.* **1969**, 885.

[2] Bleeke, J. R., Hinkle, V. P.; Rath, P. N. *Organometallics* **2001**, *20*, 1939.

[3] Bleeke, J. R.; Ortwerth, M. F.; Rohde, A. M. *Organometallics* **1995**, *14*, 2813.

[4] Bleeke, J. R.; Ortwerth, M. F.; Chiang, M. Y. *Organometallics* **1992**, *11*, 2740.

[5] Crumbie, R. L.; Ridley, D. D. *Aus. J. Chem.* **1981**, *34*, 1017.

[6] Chou, T.-S.; Tso, H.-H.; Chang, L.-J. *J. Chem. Soc., Perkin Trans 1* **1985**, 515.

[7] Burger, J. J.; Chen, T. B. R. A.; De Waard, E. R.; Huisman, H. O. *Tetrahedron* **1980**, *36*, 723.

[8] Gamero-Melo, P.; Villanueva-García, M.; Robles, J.; Paz-Sandoval, M. A. Submitted for publication.

[9] The crude yellow powders of **5** and **6** were obtained in ∼69% and 45% yield. Purification with $CHCl_3/H_2O/Et_2O$ of these products afforded **5** and **6** in 41% and 43% yield. The potassium butadienesulfinate ligand as a precursor of **5** is highly recommended for a better yield (83%).

10.1021/om040021s CCC: $27.50

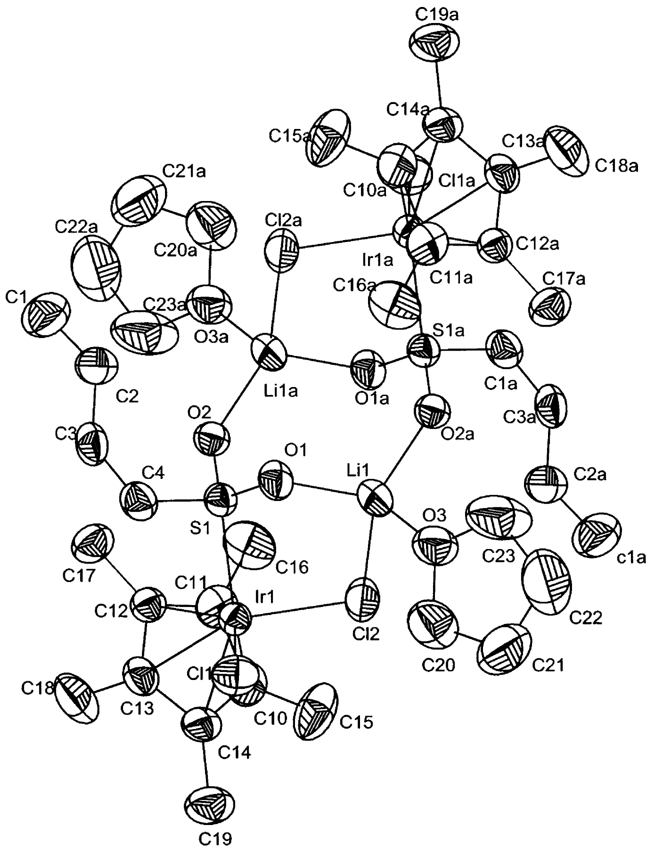
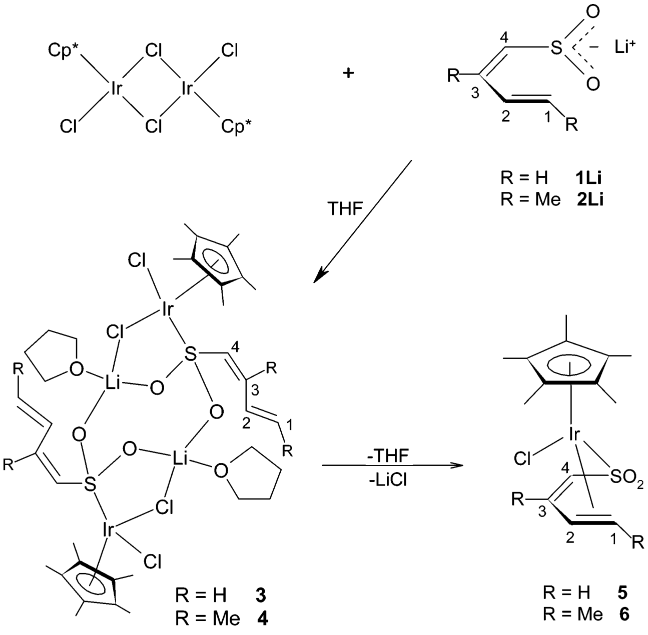


Figure 1. Molecular structure of **3**.

Scheme 2



The single-crystal X-ray analysis of the orange crystalline materials that were obtained revealed them to be the dinuclear species **3** and **4** as shown in Figures 1 and 2. These are presumed to arise from dimerization of a $Cp^*Ir(Cl)_2[(5\text{-}\eta)\text{-}SO_2CH{=}CRCH{=}CHR)](Li)(THF)$ fragment, in which only the sulfur atom of the **1Li** or **2Li** complex coordinates to the iridium metal and one of the oxygen atoms of the sulfonyl group interacts with a lithium atom. The lithium is also bonded to a chlorine atom and stabilized from a weakly coordinated solvent molecule of THF.

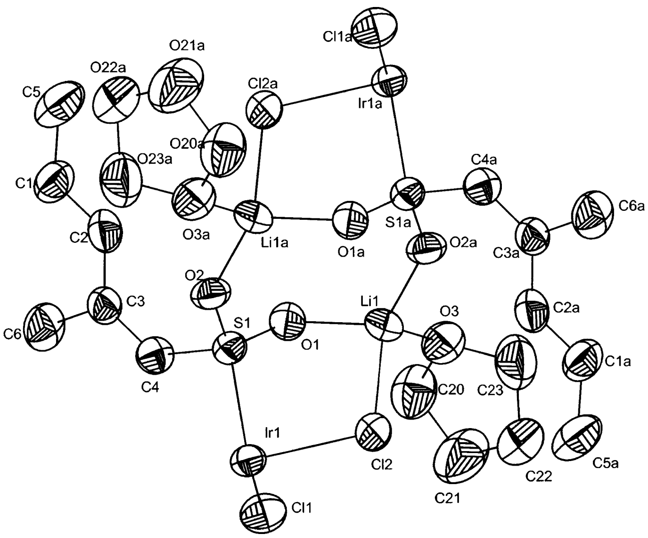


Figure 2. Molecular structure of **4**. Cp* ligand atoms have been omitted for clarity.

For compounds **3** and **4**, the crystallographic data, data collection parameters, and structure refinement details are given in Table 1, bond lengths in Table 2, and bond angles in Table 3.

The crystal structures of compounds **3** and **4** revealed the presence of two metallacyclic five-membered rings and one metallacyclic eight-membered ring. The conformation of the butadienesulfinate ligand is S-shaped, and the diene is not coordinated to the metal. The C1−C2 and C3−C4 bond distances for compounds **3** and **4** are 1.318(13), 1.333(11) and 1.308(9), 1.337(8) Å, respectively, which are typical for carbon−carbon double bonds. The carbon−sulfur bond lengths of 1.770(8) and 1.768(6) Å for **3** and **4** lie between typical C−S single bond (1.82 Å) and double bond (1.60 Å) distances.[10] The iridium−sulfur bond distances of 2.2965(17) and 2.2941(14) Å for **3** and **4** are quite short (vide infra). Almost an identical Ir−S bond distance has been reported for the "iridathiophene" complex *trans*-$C(CH_3)C(Br)CHSIr(PEt_3)_2Br_2$ [2.294(4) Å],[3] in which a substantial participation of the metal−ligand moiety in ring bonding is suggested. Contrastingly, the localized, nonaromatic, five-membered iridacycle complex *mer*-$C(CH_2)CH{=}CHSIr(PMe_3)_3H$[3] and complex $Ir[(1,2,5\text{-}\eta)\text{-}SCH{=}CHCH{=}CH_2](PMe_3)_3$[4] have normal single bond lengths of 2.441(2) and 2.417(3) Å, respectively.

^1H and ^{13}C NMR spectra taken in TDF support the structures for **3** and **4**, as shown in Scheme 2, in which an *S* conformation is observed in solution (5.19, $H1_{gem}$, 5.14, $H1'_{gem}$; 7.93, H2; 5.86, H3; 6.48, H4; $J_{1,2} = 17.2$ Hz, $J_{1',2} = 9.9$ Hz, $J_{2,3} = 11.0$ Hz, $J_{3,4} = 11.4$ Hz, for compound **3**). It might be noteworthy that the $J_{2,3} = 11.0$ Hz, $J_{3,4} = 11.4$ Hz for the corresponding single and double carbon−carbon bonds are almost identical, which may suggests a *cis,cis* coupling for a U conformer. However, the NOESY experiment confirms the *trans* and *cis* coupling of the *S* conformer, showing spatial interaction between hydrogens H4 and H3, H3 and $H1_{gem}$, and H2 and $H1'_{gem}$. The corresponding carbon resonances for C1, C2, C3, and C4 at 120.3, 133.0, 128.4,

---

(10) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry. Principles of Structure and Reactivity*; Harper Collins College Publisher, 1993; p A-30.

Table 1. Crystal Data for Iridium Compounds 3, 4, and 5

	3	**4**	**5**
	$C_{18}H_{28}Cl_2IrLiO_3S$	$C_{20}H_{32}Cl_2IrLiO_3S$	$C_{16}H_{22}Cl_7IrO_2S$
mol wt	594.50	622.56	718.75
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P21/n$	$P21/n$	$P21/c$
a (Å)	8.3875(3)	12.5492(3)	11.2901(2)
b (Å)	14.7045(5)	15.3825(4)	16.7196(3)
c (Å)	18.0380(7)	12.9700(4)	13.0005 (3)
α (deg)	90	90	90
β (deg)	98.674(2)	103.2310(1)	97.1240(10)
γ (deg)	90	90	90
V (Å^3)	2224.54(14)	2437.24(11)	2435.11(8)
Z	4	4	4
cryst size (mm)	0.25 × 0.2 × 0.15	0.1 × 0.075 × 0.05	0.3 × 0.15 × 0.15
D_{calc} (g cm^{-3})	1.775	1.697	1.960
2θ range (deg)	5.30−54.98	4.08−54.94	6.88−54.88
h, k, l ranges	$-10 \le h \le 10$	$-16 \le h \le 16$	$0 \le h \le 14$
	$-16 \le k \le 19$	$-19 \le k \le 19$	$0 \le k \le 21$
	$-22 \le l \le 21$	$-16 \le l \le 15$	$-16 \le l \le 16$
total no. data	14 830	30 254	4566
total no. unique data	4889	5538	4566
	[R(int) = 0.0710]	[R(int) = 0.1013]	[R(int) = 0.0000]
final R1	0.0461	0.0392	0.0431
final wR2	0.0798	0.0671	0.1072
GOF	1.044	1.022	1.134

Table 2. Bond Lengths (Å) of Compounds 3, 4, and 5

	3	**4**	**5**
Ir1−S1	2.2965(17)	2.2941(14)	2.3091(18)
Ir1−Cl1	2.404(2)	2.3996(16)	2.3872(17)
S1−O1	1.475(5)	1.477(4)	1.470(5)
S1−O2	1.473(5)	1.477(4)	1.465(5)
C1−C2	1.318(13)	1.308(9)	1.428(12)
C2−C3	1.425(12)	1.444(9)	1.459(13)
C3−C4	1.333(11)	1.337(8)	1.324(12)
C4−S1	1.770(8)	1.768(6)	1.774(8)
C1−Ir1			2.177(7)
C2−Ir1			2.202(7)
Ir1−Cl2	2.4120(19)	2.4121(15)	
Li1−Cl2	2.424(13)	2.368(10)	
Li1−O1	1.891(14)	1.902(11)	
Li1A−O2	1.928(13)	1.881(10)	
Li1−O3	1.976(15)	1.946(11)	
Li1−O2A	1.928(13)	1.881(10)	
O3−C20	1.406(10)	1.438(8)	
O3−C23	1.372(12)	1.419(9)	
C20−C21	1.411(15)	1.463(11)	
C21−C22	1.421(16)	1.458(12)	
C22−C23	1.442(17)	1.489(11)	
C1−C5		1.502(10)	
C3−C6		1.497(8)	

Table 3. Bond Angles (deg) of Compounds 3, 4, and 5

	3	**4**		**5**
O1−S1−Ir1	114.8(2)	115.99(17)	O1−S1−Ir1	112.6(2)
O2−S1−Ir1	111.4(2)	109.51(17)	O2−S1−Ir1	116.8(2)
O2−S1−O1	112.4(3)	111.7(2)	O2−S1−O1	112.5(3)
O1−S1−C4	104.1(4)	104.2(3)	O1−S1−C4	106.7(4)
O2−S1−C4	105.8(4)	106.9(3)	O2−S1−C4	104.5(4)
C4−S1−Ir1	107.5(3)	107.9(2)	C4−S1−Ir1	102.2(3)
S1−Ir1−Cl1	88.58(7)	89.21(6)	S1−Ir1−Cl1	88.81(6)
S1−Ir1−Cl2	87.51(6)	87.60(5)	C1−C2−C3	122.6(7)
C1−C2−C3	122.2(9)	128.2(7)	C2−C3−C4	123.2(7)
C2−C3−C4	128.8(8)	124.5(6)	C3−C4−S	116.8(7)
C3−C4−S1	128.6(7)	129.3(5)	C2−C1−Ir	70.0(4)
Cl1−Ir−Cl2	89.66(8)	89.21(6)	C2−C1−Ir	71.9(4)
O1−Li1−O3	123.3(8)	108.4(5)	C3−C2−Ir1	112.8(5)
O1−Li1−O2A	116.4(7)	122.2(6)	C1−Ir1−C2	38.1(3)
O1−Li1−Cl2	94.7(5)	96.4(4)	C1−Ir1−S1	90.5(2)
S1−O2−Li1A	134.6(5)	139.4(4)	C2−Ir1−S1	81.5(2)
S1−O1−Lil1	125.4(5)	120.9(4)	C1−Ir1−Cl1	82.6(2)
Ir1−Cl2−Li1	104.2(3)	104.7(2)	C2−Ir1−Cl1	119.1(2)

138.3 and 129.2, 130.0, 134.0, 136.7 ppm for compounds **3** and **4**, respectively, confirm that the butadiene fragment is not coordinated.

As mentioned above, compounds **3** and **4** are immediately transformed to the corresponding yellow compounds Cp*IrCl[(1,2,5-η)-$SO_2CH{=}CRCH{=}CHR$) (R = H, **5**; Me, **6**) if THF is removed. At the beginning, purification of compounds **5** and **6**, from reactions with **1Li** and **2Li**, was complicated, because the LiCl was difficult to remove completely,[11] until both complexes were washed with H_2O, obtaining these compounds in 41 and 43% yield, respectively.[9] The presence of two methyl groups in the butadienesulfinate ligand confers higher stability to compounds **4** and **6**, compared to **3** and **5**. The η^3 complexes Cp*IrCl[(1,2,5-η)-buta-1,3-dien-5-*S*-sulfinate] (**5**) and Cp*IrCl[1,3-dimethyl-(1,2,5-η)-buta-1,3-dien-5-*S*-sulfinate] (**6**) (Scheme 2) show a bonding mode that involves a localized iridium−sulfur and iridium−olefin coordination. This type of bonding has been previously observed for several iridium compounds with thiapentadienyl[3,4,11] and pentadienyl[12] ligands. It has been suggested that the stability of this bonding mode may result, in part, from the stability of d^6 Ir(III) in an octahedral coordination geometry.[12]

The bonding mode of the butadienesulfinate ligands in **5** and **6** is evident from the $^{13}C\{^1H\}$ NMR spectra, which exhibit internal uncomplexed carbon atoms C3 and C4 resonating at higher frequencies: 129.4, 153.7 and 142.1, 140.7 ppm, respectively, whereas the terminal-coordinated carbon atoms, C1 and C2, resonate at 57.4, 82.4 and 76.6, 84.8 ppm, respectively. The $^{13}C-^1H$ HETCOR NMR spectra confirm the connectivity of the corresponding carbon and hydrogen atoms.

A noticeable difference in ^{13}C NMR is observed for the corresponding quaternary carbon atoms of the Cp* ligands in compounds **5** and **6** compared to those of the precursors **3** and **4**. A significant deshielding of $\Delta\delta$ = 12.89, 12.96 follows from transformation of compound

---

(11) ^{7}Li NMR was quite useful in the identification of impurities and final purification of **5** and **6**.

(12) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Frediani, P.; Herrera, V.; Sánchez-Delgado, R. *J. Am. Chem. Soc* **1993**, *115*, 2731.

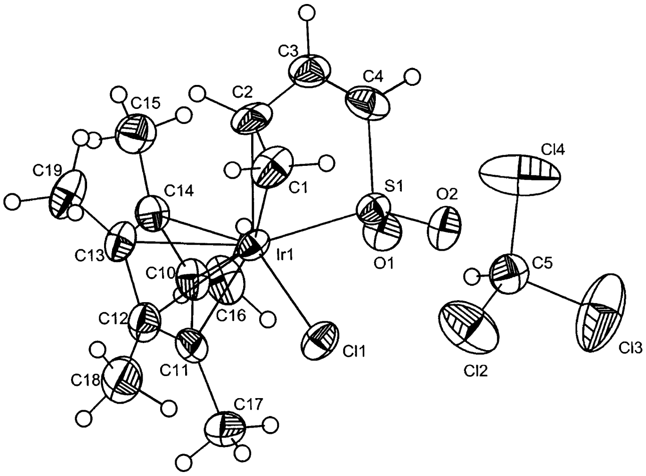


Figure 3. Molecular structure of **5**.

3 to **5** and **4** to **6**, which may reflect a significant decrease in the electron density of the iridium atoms of compounds **5** and **6**.

The methathesis reaction of $[Cp^*IrCl_2]_2$ with **1K** showed no evidence of an intermediate, such as **3**. Instead, an immediate formation of compound **5** was achieved in 83% yield. The size of the alkaline metal was crucial in the isolation of the lithium derivatives **3** and **4**. The molecular structure of compound **5** (Figure 3) confirms the bonding mode of the sulfur to the iridium atom. Two molecules of chloroform are enclosed in the crystals per each formula unit of **5**. Some of them show disorder. The corresponding crystal data for compound **5**, as well as bond lengths and angles, are given in Tables 1, 2, and 3, respectively.

The iridium–sulfur bond length of 2.3091(18) Å is quite similar to those observed for the dinuclear compounds **3** and **4** (vide supra). The C1–C2 and C3–C4 bond distances for compound **5** are 1.428(12) and 1.324(12) Å for coordinated and noncoordinated carbon–carbon double bonds, respectively. The carbon–sulfur bond length of 1.774(8) Å, as for compounds **3** and **4**, lies between a single and double C–S bond (vide supra). The sulfur–oxygen (O1 and O2) and iridium–chlorine bond lengths are 1.470(5) and 1.465(5) and 2.3872(17) Å, respectively, which are slightly shorter and shorter compared to the corresponding bond lengths in molecules **3** (1.475(5), 1.473(5) and 2.404(2) Å) and **4** (1.477(4), 1.477(4) and 2.3996(16) Å), respectively. Finally, clear evidence of the coordination of C1–C2 [1.428(12) Å] to iridium is given for compound **5**, whereas C3–C4 [1.324(12) Å] remains nonbonding. Some intermolecular interactions between compound **5** and one chloroform molecule were observed for H5···O2 (2.222 Å), H5···Cl1 (2.846 Å), whereas a second molecule of chloroform interacts with another molecule of **5** giving intermolecular interactions at H6···O1 (2.116 Å) and Cl5···H4 (2.941 Å). Other intermolecular interactions observed between two molecules of **5** were H3···Cl1 (2.679 Å), H2···O2 (2.671 Å), H2···O1 (2.694 Å), and H15···O1 (2.444 Å). All these interactions are shorter than the corresponding van der Waals radii.

Concluding Remarks

In the present study, we have synthesized and described the X-ray molecular structures of the unique intermediate iridium–lithium complexes **3** and **4**, which are easily transformed into iridium complexes **5** and **6**. The potassium butadienesulfinate **1K** with $(Cp^*IrCl_2)_2$ gives directly compound **5**, and its X-ray study confirms the iridium–sulfur and the exclusive terminal olefin coordination of the butadienesulfonyl ligand to the iridium center. The high reactivity of complexes **3** and **4** suggests that it may be possible to use them to prepare a range of mononuclear derivatives with two-electron donors, which will be promising candidates for future investigations of this novel ligand and its capability of interconversion.

Experimental Section

General Procedures. Standard inert-atmosphere techniques were used for all syntheses and sample manipulations. The solvents were dried by standard methods (diethyl ether and THF with Na/benzophenone, CH_2Cl_2 and $CHCl_3$ with $CaCl_2$) and distilled under nitrogen prior to use. Compound $[Cp^*IrCl_2]_2$ was prepared according to literature procedures.[13] All other chemicals were used as purchased from Sigma-Aldrich, Strem Chemicals, Merck, J. T. Baker, Isotec, and Cambridge Isotopes. Elemental analyses were performed at the Chemistry Department of Cinvestav with a Thermo-Finnigan Flash 112. Solution IR spectra were recorded on a Perkin-Elmer 6FPC-FT spectrophotometer using a $CHCl_3$ solution or KBr with NaCl plates. ^1H, ^{13}C, and ^7Li NMR spectra were recorded on JEOL GSX-270, JEOL Eclipse+400 MHz, or Bruker 300 MHz spectrometers in deoxygenated, deuterated solvents. ^1H and ^{13}C NMR chemical shifts are reported relative to TMS, and ^7Li NMR chemical shifts are reported relative to LiCl in H_2O. Mass spectra were obtained at Washington University, St. Louis, MO.

Synthesis of Potassium Butadienesulfinate (1K). A solution of **1** (2.5 g, 21.16 mmol) in 80 mL of THF at room temperature was stirred. Then, a mixture of *t*-BuOK (2 g, 17.82 mmol) in 10 mL of THF was added dropwise. During the addition the color changed, and a mustard-yellow precipitate was observed. After stirring 1 h at room temperature, the solid became pale yellow. The solution was evaporated under vacuum, and the residue was washed five times with THF (20 mL) and dried under vacuum. The yield of the cream solid **1K** was essentially quantitative (99.1%). This compound is soluble in DMSO and D_2O. It does not melt below 250 °C. ^1H NMR (DMSO): δ 5.14 (d, $J = 16.8$ Hz, 1H, H1), 5.08 (d, $J = 8.8$ Hz, 1H, H1′), 6.99 (m, 1H, H2), 5.97 (dd, $J = 10.3$, 9.5 Hz, 1H, H3), 5.75 (d, $J = 10.3$ Hz, 1H, H4). ^1H NMR (D_2O): δ 5.43 (d, $J = 16.7$ Hz, 1H, H1), 5.36 (d, $J = 9.9$ Hz, 1H, H1′), 7.02 (m, 1H, H2), 6.44 (dd, $J = 10.8$, 10.6 Hz, 1H, H3), 5.94 (d, $J = 10.6$ Hz, 1H, H4). $^{13}C\{^1H\}$ NMR (DMSO): 118.8 (C1), 133.4 (C2), 127.2 (C3), 153.5 (C4). $^{13}C\{^1H\}$ NMR (D_2O): δ 123.1 (C1), 131.2 (C2), 133.9 (C3), 144.2 (C4). IR (KBr): 1012 (s), 962 (s) cm^{-1}. $C_4H_5KO_2S \cdot 0.1H_2O$ (158.04): calcd C 30.40, H 3.31; found C 30.34, H 3.32.

Synthesis of Lithium Butadienesulfinate (1Li). A 1.6 M *n*-BuLi (2.65 mL, 4.23 mmol) solution was added dropwise, at −110 °C (liq N_2/EtOH), to a solution of diisopropylamine (0.6 mL, 4.23 mmol) in THF (5.3 mL), under nitrogen. The freshly prepared LDA was allowed to rise to room temperature, and after 20 min the very pale yellow solution was once again cooled to −110 °C. A solution of **1** (0.5 g, 4.23 mmol) in THF (6 mL) was transferred to the LDA solution, which turned from light yellow to red when the addition was finished. The reaction mixture was allowed to rise to room temperature, and it was stirred for 1 h. At this time the color of the suspension was yellow. The solvent was evaporated under vacuum, and

---

(13) Bleeke, J. R.; Boorsma, D.; Chiang, M. Y.; Clayton, T. W., Jr.; Haile, T.; Beatty, A., M.; Xie, Y.-F. *Organometallics* **1991**, *10*, 2391.

the residue was washed three times with THF (10 mL) and five times with EtOH (15 mL). **1Li** was partially soluble in EtOH, and the soluble fraction was recovered reducing the volume of EtOH (15 mL), adding Et_2O (80 mL), and cooling it to −5 °C for 24 h. The cream-yellow powder was filtered and dried 8 h under vacuum, obtaining 67.0% yield (0.35 g, 2.82 mmol). The solid is very soluble in DMSO and H_2O, slightly soluble in EtOH and MeOH, and insoluble in acetone, THF, Et_2O, and hexane. It does not melt below 250 °C. ESIMS: *m/z* [125.142]. ^1H NMR (D_2O): δ 5.38 (d, $J = 17.5$ Hz, 1H, H1), 5.31 (d, $J = 9.9$ Hz, 1H, H1′), 6.96 (m, 1H, H2), 6.38 (dd, $J = 11.0$, 11.0 Hz, 1H, H3), 5.89 (d, $J = 11.0$ Hz, 1H, H4). $^{13}C\{^1H\}$ NMR (D_2O): δ 123.1(C1), 131.2 (C2), 134.0(C3), 144.2 (C4). $^7Li\{^1H\}$ NMR (D_2O): δ 5.34. IR (KBr): 1029 (sh), 1008 (vs) cm^{-1}. $C_4H_5LiO_2S{\cdot}0.25H_2O$ (128.594): calcd C 37.36, H 4.30; found C 37.39, H 4.31.

Synthesis of Lithium 3,5-Dimethylbutadienesulfinate (2Li). A solution of *n*-BuLi (1.6 M in hexane, 1.06 mL, 1.71 mmol) was slowly added to a cold (−35 °C) THF (2 mL) solution of compound **2** (0.25 g, 1.71 mmol). The light brown reaction mixture was allowed to rise to room temperature and stirred 1.3 h. The solution was completely evaporated, and the remaining beige solid was washed five times with THF (5 mL) and dried under vacuum for 4 h. **2Li** was obtained as a cream solid in 88.4% yield (0.23 g, 1.51 mmol). It does not melt below 250 °C. HRESI: *m/z* 153.0562. ^1H NMR (DMSO): δ 5.63 (m, 1H, H1), 1.73(d, $J = 6.4$ Hz, 3H, Me1), 6.84 (d, $J = 15.8$ Hz, 1H, H2), 1.69 (s, 3H, Me3), 5.51 (s, 1H, H4). ^1H NMR (D_2O): δ 6.04 (m, 1H, H1), 1.79 (d, $J = 6.9$ Hz, 3H, Me1), 6.83 (d, $J = 15.3$ Hz, 1H, H2), 1.86 (s, 3H, Me3), 5.72 (s, 1H, H4). $^{13}C\{^1H\}$ NMR (DMSO): δ 125.9(C1), 18.8 (Me1), 129.8 (C2), 130.8 (C3), 19.7 (Me3), 150.0 (C4). $^{13}C\{^1H\}$ NMR (D_2O): δ 126.9 (C1), 17.9 (Me1), 132.1 (C2), 140.3 (C3), 19.0 (Me3), 139.9 (C4). $^7Li\{^1H\}$ NMR (DMSO): δ 4.30. $^7Li\{^1H\}$ NMR (D_2O): δ 5.37. IR (KBr): 984 (vs), 1012 (vs) cm^{-1}. $C_6H_9LiO_2S$ (152.140): calcd C 47.37, H 5.96; found C 47.64, H 6.20.

Synthesis of $[Cp^*Ir(Cl)_2(SO_2CH{=}CRCH{=}CHR)(Li)(THF)]_2$ (R = H, 3; Me, 4). Compound $(Cp^*IrCl_2)_2$ (100 mg, 0.125 mmol) was dissolved in 10 mL of THF solution to form an orange solution and cooled at −110 °C (liq N_2/EtOH). Then, compound **1Li** (32 mg, 0.25 mmol) or **2Li** (38.2 mg, 0.25 mmol) suspended in THF (8 mL) was added dropwise. As the addition proceeded, the cream solid disappeared and a clear (yellow, **3**; orange-yellow, **4**) solution was observed after 2 h at room temperature. The solution was filtered and the volume reduced until 4 mL, diethyl ether was added (80 mL), and after cooling the solution at −5 °C some small orange crystals precipitated along with a yellow powder.[9] The crystals were filtered and separated manually from the yellow powder. The orange crystals of **3** were obtained in ~17% yield (26 mg, 0.043 mmol). It does not melt below 300 °C. ^1H NMR (TDF): δ 5.14 (d, $J = 9.9$ Hz, 1H, $H1'_{gem}$), 5.19 (dd, $J = 17.2$, 2.2 Hz, 1H, $H1_{gem}$), 7.93 (dt, $J = 11.0$, 17.2 Hz, 1H, H2), 5.86 (dd, $J = 11.0$, 11.4 Hz, 1H, H3), 6.48 (d, $J = 11.4$ Hz, 1H, H4), 1.54 (s, 15H, Cp), 3.59 (m, THF), 1.74 (m, THF). $^{13}C\{^1H\}$ NMR (TDF): δ 120.3 (C1), 133.0 (C2), 128.4 (C3), 138.3 (C4), 7.5 (Cp*), 90.1 (Cp*), 66.9 (THF), 24.8 (THF). ^7Li NMR (TDF): δ 5.22. Compound **4**: 45% (70 mg, 0.113 mmol). It does not melt below 300 °C. ^1H NMR (TDF): δ 5.80 (dq, $J = 6.4$, 13.2 Hz, 1H, H1), 1.78 (d, $J = 6.6$ Hz, 3H, Me1), 7.88 (d, $J = 14.7$ Hz, 1H, H2), 1.81 (s, 3H, Me3), 6.34 (s, 1H, H4), 1.51 (s, 15H, Cp*), 3.59 (m, THF), 1.74 (m, THF). $^{13}C\{^1H\}$ NMR (TDF): δ 129.2 (C1), 19.1 (Me1), 130.0 (C2), 134.0 (C3), 20.0 (Me3), 136.7 (C4), 8.7 (Cp*), 91.1 (Cp*), 66.9 (THF), 24.8 (THF). ^7Li NMR (TDF): δ 3.44. IR (KBr): 1051 (vs), 1123 (s), 1163 (s), 1195 (s), 1380 (s), 1443 (vs), 1496 (sh), 1580 (s), 1639 (vs) cm^{-1}. $C_{40}H_{64}Cl_4Ir_2O_6S_2Li_2{\cdot}0.75LiCl$ (1276.97): calcd C 37.62, H 5.05; found C 37.52, H 5.09.

Synthesis of $Cp^*Ir(Cl)(SO_2CH{=}CHCH{=}CH_2)$ (5). Compound $(Cp^*IrCl_2)_2$ (170 mg, 0.21 mmol) was dissolved in 10 mL of THF solution to form an orange solution and cooled at −110 °C (liq N_2/EtOH). Then, compound **1K** (67 mg, 0.43 mmol) suspended in THF (8 mL) was added dropwise. As the addition proceeded, the cream solid disappeared and a clear yellow solution was observed after 2 h at room temperature. The solution was filtered and the solvent evaporated under vacuum. After cooling the solution at −5 °C, recrystallization from chloroform/diethyl ether afforded a yellow powder. Addition of diethyl ether to the concentrated chloroform solution gave 170 mg (0.35 mmol, 83% yield). Compound **5** does not melt below 300 °C. HRESI: *m/z* 481.0587. ^1H NMR ($CDCl_3$): δ 3.83 (d, $J = 12.4$ Hz, 1H, H1), 3.91 (d, $J = 9.5$ Hz, 1H, H1′), 5.13 (m, 1H, H2), 5.59 (dd, $J = 2.2$, 6.6 Hz, 1H, H3), 6.56 (d, $J = 6.6$ Hz, 1H, H4), 1.78 (s, 15H, Cp*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 57.4 (C1), 82.4 (C2), 129.4 (C3), 153.7 (C4), 8.5 (Cp*), 103.0 (Cp*). IR ($CHCl_3$): 811 (s), 1027 (w), 1062 (vs), 1115 (m), 1203 (vs), 1224 (s), 1298 (m), 1381 (m), 1458 (m, br), 1628 (w) cm^{-1}. IR (KBr): 746 (m), 814 (m), 1030 (vs), 1053 (vs), 1118 (m), 1161 (s), 1224 (s), 1184 (s), 1299 (m), 1455 (s), 1638 (vs,br), cm^{-1}. $C_{14}H_{20}ClIrO_2S$ (480.0): calcd C 35.03, H 4.20; found C 35.22, H 4.31.

Synthesis of $Cp^*Ir(Cl)(SO_2CH{=}CMeCH{=}CHMe)$ (6). Compound **6** was obtained following a procedure identical to that for **5**, starting from $(Cp^*IrCl_2)_2$ (100 mg, 0.13 mmol) and **2Li** (38.2 mg, 0.25 mmol), affording an orange-yellow solution, which after treatment gave a yellow powder. This powder was dissolved in $CHCl_3$ (5 mL), washed with H_2O (2 mL), and dried over Na_2SO_4. Addition of diethyl ether to the concentrated chloroform solution gave 55 mg (0.11 mmol, 43% yield). Mp: 162−165 °C (dec). HRESI: *m/z* 509.0913. ^1H NMR ($CDCl_3$): δ 5.03 (dq, $J = 6.2$, 11.4 Hz, 1H, H1), 1.90 (d, $J = 6.3$ Hz, 1H, Me1), 4.52 (d, $J = 11.3$ Hz, 1H, H2), 2.18 (s, 3H, Me3), 6.04 (s, 1H, H4), 1.75 (s, 15H, Cp*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 76.6 (C1), 18.2 (Me1), 84.8 (C2), 142.1 (C3), 19.9 (Me3), 140.7 (C4), 9.4 (Cp*), 104.0 (Cp*). IR ($CHCl_3$): 712 (vs), 733 (vs), 913 (vs), 1025 (sh), 1061 (s), 1120 (m), 1203 (s), 1379 (m), 1445 (m) cm^{-1}. IR (KBr): 797 (m), 827 (m), 1056 (vs), 1120 (s), 1200 (sh), 1203 (vs), 1256 (m), 1379 (vs), 1443 (vs,br), 1506 (sh), 1637 (vs,br) cm^{-1}. $C_{16}H_{24}ClIrO_2S{\cdot}0.1CHCl_3$ (520.02): calcd C 37.19, H 4.67; found C 37.19, H 4.72.

Crystal Structure Determinations of 3, 4, and 5. Crystals suitable for X-ray diffraction were obtained by cooling a concentrated THF/Et_2O solution of **3** and **4** to −5 °C. Yellow prism crystals were mounted on a glass fiber using perfluorpolyether oil. The structures consist of one molecule of **3** and **4** per asymmetric unit. Single crystals of **5** were obtained by recrystallization from chloroform/hexane at −20 °C. X-ray diffraction measurements were made at 203 K, on a Enraf Nonius-KappaCCD diffractometer, using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods using SHELXS-97[15a] included in the package Wingx[15b] and refined by a full-matrix least-squares method based on F^2. Extinction correction was performed with SHELXL-97.[15a] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were refined isotropically in geometrically calculated positions. Crystal data, data collection parameters, and structure refinement details are summarized in Table 1. Further details of the crystal structure determinations are available from the Cambridge Crystallographic Data Center on OM040021s.CIF for compounds **3** and **4** and on quoting the depository number 234878 for **5**.

Acknowledgment. Financial support for this work was provided by Conacyt, Mexico (38507-E and 26352-

---

(14) White, C.; Yates, A.; Maitlis, P. M. *Inorg. Synth.* **1992**, *29*, 228.

(15) (a) Sheldrick, G. M. ***SHELXL***, Program for Crystal Structure Refinement; University of Göttingen: Göttingen, Germany, 1998. (b) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.

E). E.S.C., A.R.M., and P. G. M. thank Conacyt for scholarships. P. G. M. also thanks IMP for financial support. We thank the service of the Washington University Mass Spectrometer Resource, which is supported by the NIH Center for Research Resources. We thank Dr. Armando Ariza Castolo and Victor González for assistance with some NMR experiments.

Supporting Information Available: Tables giving crystallographic data, bond lengths, and bond angles for compounds **3**–**5** and a figure giving ^{1}H NOESY of compound **3**; crystallographic data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

OM040021S