Table I. Selected Bond Lengths (Å) and Bond Angles (deg) for the [PPN][W(CO)$_4$(η^2-S$_2$CCH$_3$)] Complex[a]

Bond Lengths			
W(1)-S(1)	2.557 (5)	S(2)-C(1)	1.71 (2)
W(1)-S(2)	2.565 (5)	C(1)-C(2)	1.47 (3)
W(1)-C(3)	1.99 (2)	C(3)-O(3)	1.17 (2)
W(1)-C(4)	1.93 (2)	C(4)-O(4)	1.19 (2)
W(1)-C(6)	1.94 (2)	C(5)-O(5)	1.21 (2)
W(1)-C(5)	1.91 (2)	C(6)-O(6)	1.17 (2)
S(1)-C(1)	1.67 (2)		
Bond Angles			
S(1)-W(1)-S(2)	67.0 (1)	S(1)-W(1)-C(4)	95.3 (6)
S(2)-W(1)-C(3)	90.7 (6)	S(1)-C(1)-S(2)	113.4 (10)

[a] The values listed are for only one of the two molecules that crystallized in the unit cell.

sentative listing of bond lengths and bond angles is presented in Table I.

[W(CO)$_4$(η^2-S$_2$CCH$_3$)]$^-$ was found to react with added CO to yield the pentacarbonyl species, although the reaction is much slower than the corresponding reaction involving [W(CO)$_4$(η^2-O$_2$CCH$_3$)]$^-$.[10] Whereas the latter reacts with CO at ambient temperature to yield the monodentate species in a few minutes, after 2 days the reaction between [W(CO)$_4$(η^2-S$_2$CCH$_3$)]$^-$ and CO has not gone to completion. The slower reactivity of the sulfur analogues is anticipated on the basis of ring strain and bond strength considerations. The thermal and photochemical reactions of [W(CO)$_5$CH$_3$]$^-$ and CS$_2$ are summarized in Scheme I.

The photoenhanced carbon–carbon bond-forming reaction of CS$_2$ with [W(CO)$_5$CH$_3$]$^-$ is most likely initiated by W–CH$_3$ homolysis (Scheme II)[13] and not CO photodissociation. Consistent with this proposal, an analogous photolyzed reaction of [W(CO)$_5$CH$_3$]$^-$ in THF in the presence of an excess of CH$_2$Cl$_2$ quantitatively afforded [W(CO)$_5$Cl]$^-$. Hence, radical pathways initiated by light analogous to those seen in SO$_2$ insertion reactions with alkyl cobaloximes may be operative.[14] Of more importance to our primary interest is the analogous behavior of CO$_2$ toward [W(CO)$_5$CH$_3$]$^-$ in the presence of light. Indeed, we have observed that the reactivity of [W(CO)$_5$CH$_3$]$^-$ toward carbon dioxide is greatly enhanced upon photolysis. However, in this instance the product is not the acetate complex but instead the product of hydrogen atom abstraction; i.e., the formate derivative [W(CO)$_5$O$_2$CH]$^-$ was afforded in good yield.[15] It is apparent from these preliminary findings that the photophysics and photochemistry of group 6 metal alkyls with CO$_2$, and the analogous heteroallene CS$_2$, warrant thorough investigation.

Scheme II

$$CH_3W(CO)_5^- \overset{h\nu}{\rightleftharpoons} CH_3^{\bullet} + {}^{\bullet}W(CO)_5^-$$

$${}^{\bullet}W(CO)_5^- + CS_2 \rightarrow (CO)_5WCS_2^{\bullet -}$$

$$(CO)_5WCS_2^{\bullet -} + CH_3W(CO)_5^- \rightarrow (CO)_4WS_2CCH_3^- + {}^{\bullet}W(CO)_5^- + CO$$

Acknowledgment. The financial support of this research by the National Science Foundation (Grant CHE 88-17873) and the Robert A. Welch Foundation is greatly appreciated.

Supplementary Material Available: Tables of refined anisotropic thermal parameters, final fractional coordinates, and thermal parameters for hydrogen atoms (5 pages); a listing of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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(13) For reports of photolytic homolysis of the closely related RMn(CO)$_5$ derivatives, see e.g.: (a) Hudson, A.; Lappert, M. F.; Lednor, P. W.; Nicholson, B. K. *J. Chem. Soc., Chem. Commun.* **1974**, 966. (b) Hudson, A.; Lappert, M. F.; Lednor, P. W.; Macquitty, J. J.; Nicholson, B. K. *J. Chem. Soc., Dalton Trans.* **1981**, 2159. (c) Young, K. M.; Wrighton, M. S. *J. Am. Chem. Soc.* **1990**, *112*, 157.

(14) Crease, A. E.; Johnson, M. D. *J. Am. Chem. Soc.* **1978**, *100*, 8013.

(15) The formate complex was conclusively identified in solution by infrared spectroscopy and, more importantly, ^{13}C NMR spectroscopy, where the –O$_2$CH resonance was found at 168.8 ppm, W–CO (cis) at 201.4 ppm, and W–CO (trans) at 206.5 ppm in acetone.[8] In addition the formate proton signal was observed at 7.90 ppm in THF.

Formation of Acetylplatina(IV)cyclobutane: Methodology for the Synthesis of Platina(IV)cyclobutane Complexes Bearing Electrophilic Substituents

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Received February 20, 1990

Summary: A methodology for the syntheses of platina(IV)cyclobutanes bearing an electron-withdrawing keto group has been achieved. This method, which involves protection of cyclopropyl methyl ketone, platinum insertion, and subsequent deprotection, yields acetylplatinacyclobutane.

Metallacyclobutane complexes range from proposed transition states to stable entities and are considered to be important pathway components in several organic transformations.[1-4] Platina(IV)cyclobutanes are among the most stable and studied. Formation of platinacyclobutanes is easily accomplished by the insertion (oxidative addition) of platinum into the carbon–carbon bond of a cyclopropane. However, until now the ring-bearing substitutions were unfortunately *limited* to alkyl and aryl groups. *The presence of strong electron-withdrawing substituents prevented insertion and thus exploration of potentially rich chemistry*[5] (eq 1). We now wish to report

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(1) Puddephatt, R. J. *Coord. Chem. Rev.* **1980**, *33*, 149.

(2) Johnson, T. H.; Cheng, S. S. *Synth. Commun.* **1980**, *10*, 381.

(3) Parshall, G. W. *Homogeneous Catalysis*; Wiley: New York, 1980.

(4) Shrock, R. R. *J. Organomet. Chem.* **1986**, *300*, 249.

(5) Powell, K. G.; McQuillin, F. J. *Tetrahedron Lett.* **1971**, *36*, 3313. McQuillin, F. J.; Powell, K. G. *J. Chem. Soc., Dalton Trans.* **1972**, 2123.

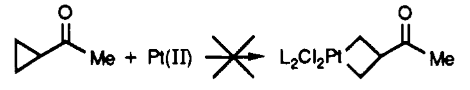
0276-7333/91/2310-0008$02.50/0

Table I. ^{13}C NMR Data for **2**–**6**[a]

atom no.[c]	**2**	**3**	**4**	**5**	**6**
1	−10.6 (349)[b]	−12.5 (364)	−10.4 (328)	−12.5 (358)	−12.4 (357)
2	50.5 (95)	55.9 (103)	30.5 (107)	49.7 (98)	55.0 (99)
3	111.6 (57)	209.4 (55)	3.2 (351)	109.0 (59)	210.3 (52)
4	20.9 (0)	26.1 (0)	211.3 (48)	19.0 (0)	26.1 (0)
5	65.0 (0)		29.7	62.9 (0)	

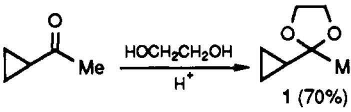
[a] Relative to $CDCl_3$; δ values are in ppm. [b] J_{PtC} (in hertz) in parentheses. [c] See numbering given in eqs 3 and 4.

a successful methodology for synthesis of platina(IV)-cyclobutanes of the type shown in eq 1.



(1)

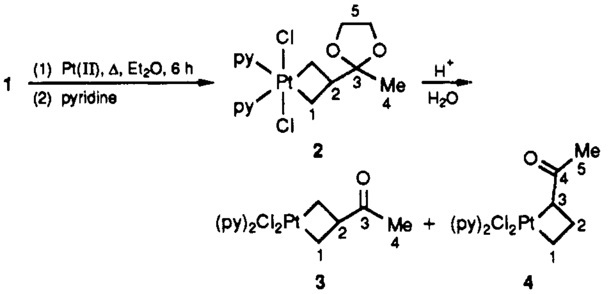
Formation of ketal **1** was accomplished in good yields under standard conditions (eq 2).[6,7] Subsequent reaction of **1** with Zeise's dimer $(C_2H_4PtCl_2)_2$ in refluxing ether yielded a yellow precipitate, which on addition of 2 equiv of pyridine in $CDCl_3$ gave only one regioisomer, **2**, in near-quantitative yields. Shaking of **2** in $CHCl_3$ and *p*-TsOH provided a mixture of **3** and **4** in quantitative yield.[9] Table I lists the ^{13}C NMR data for **2**–**4**. The ratio of **3** and **4** (1.5:1) was deduced by integration of the ^{13}C and ^1H NMR spectra.[10] Comparison of **2** and **3** to similar platinacyclobutanes in the literature gave excellent correlations.[11] Bands at 1683.3 and 1700.9 cm^{-1} in the IR spectra corroborated the carbonyl portion of **3** and **4**.



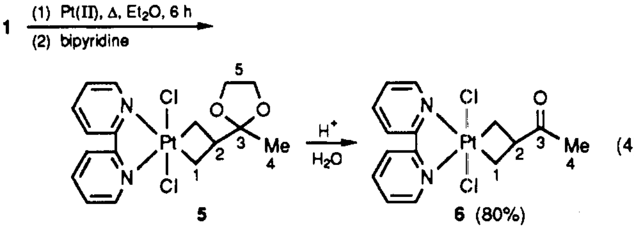
1 (70%)

(2)

Prevention of the apparent isomerization[12] during the hydrolysis step was achieved with the bidentate ligand 2,2′-bipyridine (eq 4). This ligand obviously keeps the platinum coordinatively saturated and prevents the Puddephatt rearrangement.[1] Formation of **5** followed by hydrolysis gave a single isomer, **6**. ^{13}C NMR data[13] for **5** and **6** is also listed in Table I. Again, a stretching frequency at 1700 cm^{-1} in the IR spectrum gave additional evidence for **6**.



(3)



(4)

In summary, a procedure for the synthesis of the heretofore unknown platinacyclobutanes bearing strong electron-withdrawing groups has been achieved. Further work is now underway on the chemistry of these systems.

Acknowledgment. Support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation, and Johnson-Matthey is gratefully acknowledged.

Supplementary Material Available: Experimental details for each compound, tables of ^1H, ^{13}C, and ^{195}Pt NMR data, and proton, carbon, and platinum NMR spectra for **2**–**6** (15 pages). Ordering information is given on any current masthead page.

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(6) Fevig, T. L.; Elliott, R. L.; Curran, D. P. *J. Am. Chem. Soc.* **1988**, *110*, 5064.

(7) ^1H NMR (300 MHz, $CDCl_3$: δ 3.81 (s, 4 H), 1.25 (s, 3 H), 1.0 (m, 1 H), 0.3 (m, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 109.1 (s), 64.9 (t), 24.3 (q), 18.4 (d), 1.1 (t). MS: *m/e* 128, 113, 87, 85, 69, 55, 43.

(8) Decomposition of the precipitate occurs within 3 h.

(9) Complex **2** was shaken in 3 mL of $CHCl_3$ and 1 g of *p*-TsOH in 2 mL of H_2O for 10 min. Layers were separated, and the $CHCl_3$ layer was washed with 2 mL of $NaHCO_3$ and 2 mL of brine, dried ($MgSO_4$), and concentrated.

(10) ^1H NMR (300 MHz, $CDCl_3$): **2**, δ 3.91 (s, H-5), 3.14 (t, $J_{HH} = 9.5$, $J_{PtH} = 37.3$ Hz, H-2), 2.74 (dd, $J_{HH} = 9.5, 4.4$, $J_{PtH} = 79.8$), 1.23 (s, H-4); **3**, δ 3.76 (t, $J_{HH} = 9.3$ Hz, H-2), 2.93 (dd, $J_{HH} = 9.3, 4.8$, $J_{PtH} = 80.5$ Hz, H-1), 2.64 (dd, $J_{HH} = 9.3, 4.8$, $J_{PtH} = 83.8$ Hz, H-1), 2.1 (s, H-4); 4, δ 4.50 (dd, $J_{HH} = 6.2$, $J_{PtH} = 108.1$ Hz, H-3), 3.24 (m, H-2), 2.90 (m, $J_{PtH} = 72.0$ Hz, H-1), 2.61 (m, $J_{PtH} = 81.6$ Hz, H-1), 2.52 (m, H-2), 1.55 (s, H-5). ^{195}Pt (53.7 MHz): **2**, δ 3326; **3**, δ 3441; **4**, δ 3307 (relative to external $Na_2Pt(CN)_4$).

(11) Puddephatt, R. J.; Quyser, M. A.; Tipper, C. F. H. *J. Chem. Soc., Chem. Commun.* **1976**, *16*, 626. ^{13}C NMR for $(py)_2Cl_2PtC^1H_2(Ph)C^3H_2$ (δ): C^1, −4.9 ($J_{PtC} = 369$ Hz); C^2, 48.1 ($J_{PtC} = 100.5$ Hz). ^{13}C NMR for $(py)_2Cl_2PtC^1H_2C^2H_2C^3H(Ph)$ (δ): C^1, −11.3 ($J_{PtC} = 354$ Hz); C^2, 35.1 ($J_{PtC} = 112$ Hz); C^3, 5.6 ($J_{PtC} = 326$ Hz).

(12) For a discussion on isomerization in platinacyclobutanes, see ref 1.

(13) ^1H NMR (300 MHz, $CDCl_3$): **5**, δ 4.00 (s, H-5), 3.24 (t, $J_{HH} = 9.5$, $J_{PtH} = 36.0$ Hz, H-2), 2.67 (dd, $J_{HH} = 9.4, 4.3$, $J_{PtH} = 80.1$ Hz, H-1), 2.50 (dd, $J_{HH} = 9.2, 4.3$, $J_{PtH} = 72.0$ Hz, H-1), 1.32 (s, H-4), **6**, δ 3.84 (t, $J_{HH} = 8.6$ Hz, J_{PtH} = unres, H-2), 2.87 (dd, $J_{HH} = 8.6, 4.3$, $J_{PtH} = 80.0$ Hz, H-1), 2.69 (dd, $J_{HH} = 8.6, 4.3$, $J_{PtH} = 84.6$ Hz, H-1), 2.17 (s, H-4). ^{195}Pt (53.7 MHz): **5**, δ 2910; **6**, δ 3118 (relative to external $Na_2Pt(CN)_4$).