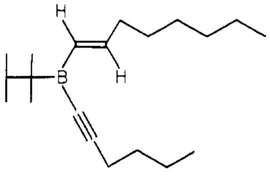
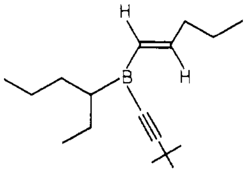
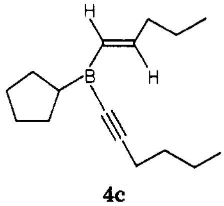
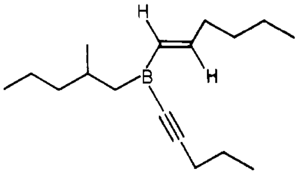
ters react with alkynyllithium reagents to generate the corresponding "ate" complexes (**7**), readily converted by 1.33 equiv of $BF_3 \cdot OEt_2$ to the desired alkylalkenylalkynylboranes in excellent yield (eq 5).

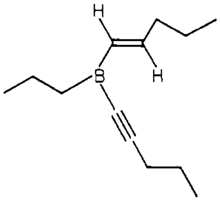
The variety of alkylalkenylalkynylboranes (**4a–h**) were prepared in excellent yields (Table I).

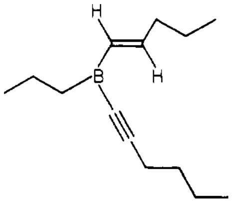

4a

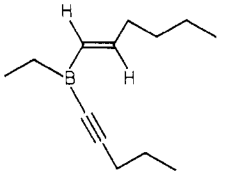

4b

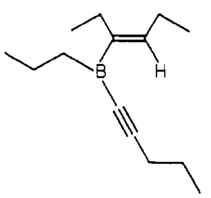

4c


4d


4e


4f


4g


4h

The following procedure for the preparation of ethyl((*E*)-1-hexenyl)(1-pentynyl)borane (**4g**) is representative. To 7.86 g of ethyldibromoborane–dimethyl sulfide[9] (30 mmol) were added 3 mL of SMe_2 and 20 mL of Et_2O, followed by a slow addition of $LiAlH_4$ in Et_2O (7.5 mmol) at 0 °C with stirring under nitrogen.[3] The reaction mixture was allowed to proceed for 3 h at 0 °C and 1 h at 25 °C. The resulting ethylbromoborane was slowly transferred to a solution of 1-hexyne (30 mmol) in Et_2O and stirred 1 h each at 0 and 25 °C. Then the reaction mixture was cooled to −10 °C and methanol (5 mL) was added. Stirring was continued for 0.25 h at −10 °C. ^{11}B NMR indicated that methyl ethylhexenylborinate was contaminated with 5–10% of diethyl ethylboronate.[10] Solvents were removed under reduced pressure, and careful distillation afforded 100% pure methyl ethyl ((*E*)-1-hexenyl)borinate (3.92 g, 25.5 mmol) in 85% yield: bp 64–66 °C (4.5 mm); ^{11}B NMR ($CDCl_3$, $BF_3 \cdot OEt_2$) δ 47.0.

To this distilled methyl ethylhexenylborinate (25.5 mmol) in THF at 0 °C was added 25.5 mmol of 1-pentynyllithium, prepared from 1-pentyne (25.5 mmol) and *n*-BuLi (25.5 mmol) in THF, and the mixture was immediately cooled to −78 °C. After 0.5 h, $BF_3 \cdot OEt_2$ (33.9 mmol) was added at −78 °C and stirred for an additional 0.5 h at −78 °C. The reaction mixture was then allowed to warm up to room temperature while the solvents were removed under reduced pressure. Pentane (25 mL) was added to the white solid and the mixture stirred for a few minutes. Pentane solution was decanted, the solid was washed with pentane (2 × 15 mL), and the pentane solution was combined. The pentane was removed under vacuum, and distillation afforded 4.17 g of 99% pure ethyl((*E*)-1-hexenyl)(1-pentynyl)borane (**4g**) (86%) (an overall yield of 73% based on ethyldibromoborane): bp 58–60 °C (0.05 mm); ^{11}B NMR ($CDCl_3$, $BF_3 \cdot OEt_2$) δ 62.0; ^1H NMR ($SiMe_4$) δ 0.7–2.00 (m, 17 H), 2.01–2.66 (m, 4 H), 6.0–7.33 (m, 2 H); IR ($CDCl_3$) 2171 ($C{\equiv}C$), 1612 cm^{-1} ($C{=}C$).

Thus, this procedure represents the first general synthesis of alkylalkenylalkynylboranes, valuable synthons, in excellent yields. We have successfully utilized thexylalkenylalkynylboranes for the synthesis of conjugated (*E*)-enynes.[11] We are presently exploring the possibilities of utilizing these fascinating organoboranes in organic transformations.

Registry No. **3** (R = thexyl), 86942-49-6; **3** (R = 3-hexyl), 86942-51-0; **3** (R = cyclopentyl), 86942-53-2; **3** (R = 2-methyl-1-pentyl), 86942-55-4; **3** (R = *n*-propyl), 86942-57-6; **3** (R = ethyl), 86942-59-8; (*E*)-**4a**, 86942-60-1; (*E*)-**4b**, 86942-61-2; (*E*)-**4c**, 86942-62-3; (*E*)-**4d**, 86942-63-4; (*E*)-**4e**, 86942-64-5; (*E*)-**4f**, 86942-65-6; (*E*)-**4g**, 86942-66-7; (*E*)-**4h**, 86942-67-8; (*E*)-**6** (R = thexyl, R^1 = H, R^2 = *n*-C_6H_{13}), 86942-68-9; (*E*)-**6** (R = 3-hexyl, R^1 = H, R^2 = *n*-C_3H_7), 86942-69-0; (*E*)-**6** (R = cyclopentyl, R^1 = H, R^2 = *n*-C_3H_7), 86942-70-3; (*E*)-**6** (R = 2-methyl-1-pentyl, R^3 = R^2 = *n*-C_4H_9), 86942-71-4; (*E*)-**6** (R = R^2 = *n*-C_3H_7, R^1 = H), 86942-72-5; (*E*)-**6** (R = Et, R^1 = R^2 = *n*-C_4H_9), 86942-73-6; (*E*)-**6** (R = *n*-C_3H_7, R^1 = R^2 = Et), 86942-74-7; $LiC{\equiv}C$-*n*-C_4H_9, 17689-03-1; $LiC{\equiv}C$-*t*-C_4H_9, 37892-71-0; $LiC{\equiv}C$-*n*-C_3H_7, 18643-50-0; $EtBBr_2 \cdot SMe_2$, 86942-75-8; 1-octyne, 629-05-0; 1-pentyne, 627-19-0; 1-hexyne, 693-02-7; 3-hexyne, 928-49-4; diethyl ethylboronate, 53907-92-9.

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[9] Ethyldibromoborane–dimethyl sulfide was prepared via redistribution of triethylborane with boron tribromide catalyzed by $BH_3 \cdot SMe_2$. For experimental details, see: Brown, H. C.; Basavaiah, D.; Bhat, N. G. *Organometallics*, in press.

[10] Diethyl ethylboronate (5–10%) was formed due to ether cleavage by $EtBBr_2$ during the hydridation step. For details, see ref 2.

[11] Brown, H. C.; Basavaiah, D.; Bhat, N. G., manuscript in preparation.

[12] Alkyldibromoboranes (except ethyl- and propyldibromoboranes) were prepared according to known procedure: Brown, H. C.; Ravindran, N.; Kulkarni, S. U. *J. Org. Chem.* **1980**, *45*, 384. Ethyl- and propyldibromoboranes were prepared as mentioned in ref 9.

[13] Brown, H. C.; Sikorski, J. A.; Kulkarni, S. U.; Lee, H. D. *J. Org. Chem.* **1982**, *47*, 863.

Evaluation by ESCA of the Electronic Effect of Methyl Substitution on the Cyclopentadienyl Ligand. A Study of Titanocenes, Zirconocenes, Hafnocenes, and Ferrocenes

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Summary: ESCA studies of a series of titanocenes, zirconocenes, hafnocenes, and ferrocenes have shown that substitution of methyls for hydrogens on the cyclopentadienyl ligand results in a dramatic electronic effect as reflected by the binding energies of the inner-shell

electrons of the metal. The substitution of two pentamethylcyclopentadienyl groups for cyclopentadienyl ligands is approximately equivalent to a one-electron reduction of the complexed metal.

Since its first general use as a ligand,[1] the pentamethylcyclopentadienyl moiety has attracted considerable attention and widespread use.[2] It is commonly known that replacement of the cyclopentadienyl group (Cp) by the pentamethylcyclopentadienyl ligand (Cp*) in certain bis- and mono(cyclopentadienyl) complexes of transition metals results in significant changes in chemical reactivity,[2,3] stability,[4] sensitivity to oxidation,[5] and many other properties.[2] This unusually major effect of methyl substitution has been attributed to both the electronic and the steric changes that accompany the replacement of a hydrogen by a methyl group. We now report a detailed ESCA[6-8] study which clearly demonstrates that an extremely large change in electronic effect occurs when a Cp ligand is replaced by a Cp* ligand.

As part of a general study aimed at the establishment of binding energy standards for titanium in connection with the use of ESCA in the study of Ziegler–Natta catalysis, we measured the values shown in Table I. In view of the large change in binding energies for the titanocene dichlorides (0.8 eV), we determined the binding energies for the corresponding fluorides and bromides and found the changes that occurred on complete methyl substitution to be comparable (0.8 and 0.9 eV, respectively). This systematic decrease in binding energy was also observed for the zirconocenes and hafnocenes, although it was slightly diminished for the series of hafnocenes. In order to evaluate the role of the pseudotetrahedral (bent sandwich) structures of the titanocene family on binding energies, we also studied the ferrocenes. Replacement of the Cp ligands by the Cp* ligands again resulted in a 0.9-eV decrease in binding energy for the Fe($2p_{3/2}$) electron. Thus, the observed changes in binding energy of the inner-shell electrons on the metal were not a function of the specific structure but rather were solely dependent on the degree of methyl substitution within a given family of compounds.

Table I. Binding Energies and Oxidation Potentials for a Series of Titanocenes, Zirconocenes, Hafnocenes, and Ferrocenes

compd[a]	binding energy (± 0.1 eV)		oxidn potential (± 0.02 V)[b]
	Ti($2p_{3/2}$)[c]	Ti($2p_{1/2}$)	$E_{1/2}$[f]
Cp_2TiF_2	457.5	463.6	1.62
$CpCp^*TiF_2$	457.0	463.1	1.24
$Cp^*_2TiF_2$	456.7	462.7	1.02
Cp_2TiCl_2	456.9	463.0	1.75
$CpCp^*TiCl_2$	456.6	462.7	1.46
$Cp^*_2TiCl_2$	456.1	462.2	1.22[h]
Cp_2TiBr_2	456.8	462.9	1.70
$CpCp^*TiBr_2$	456.5	462.6	1.44
$Cp_2^*TiBr_2$	455.9	462.0	1.21
	Zr($3d_{5/2}$)[c]	Zr($3d_{3/2}$)	$E_{1/2}$[f]
Cp_2ZrCl_2	181.9	184.2	1.84
$CpCp^*ZrCl_2$	181.5	183.9	1.43
$Cp^*_2ZrCl_2$	181.1	183.5	1.22
	Hf($4f_{7/2}$)[c]	Hf($4f_{5/2}$)	$E_{1/2}$[f]
Cp_2HfCl_2	17.1	18.6	1.79
$CpCp^*HfCl_2$	16.8	18.4	1.43
$Cp^*_2HfCl_2$	16.5	18.1	1.28
	Fe($2p_{3/2}$)[d]	Fe($2p_{1/2}$)	$E^{\circ\prime}$[g]
Cp_2Fe	708.0	720.7	0.31
$CpCp^*Fe$	707.6	720.3	0.04
Cp^*_2Fe	707.1[e]	719.8	−0.23
$[CpFe(CO)_2]_2$	708.1	720.9	0.54[i]
$[Cp^*Fe(CO)_2]_2$	707.7	720.5	0.21[i]

[a] Cp = C_5H_5; Cp* = $C_5(CH_3)_5$. [b] Evaluated by single sweep cyclic voltammetry at 22 °C with solutions which were ca. 10^{-3} M in substrate. Scan rates were 100 mV/s. A saturated NaCl–SCE was used as the reference electrode, and a platinum bead was the working electrode. The supporting electrolyte was 0.1 N tetra-*n*-butylammonium perchlorate. Potentials were referred to the ferrocene/ferrocenium couple ($E^\circ = 0.31$ V by definition). [c] Runs made at 23 °C. [d] Measured at −196 °C. [e] Measured at both 23 and −196 °C. The same value was obtained at both temperatures. [f] $E_{1/2}$ are reported for irreversible oxidations in acetonitrile. [g] $E^{\circ\prime}$ are reported for reversible oxidations in methylene chloride where $E^{\circ\prime} = (E_p^{ox.} + E_p^{red.})/2$ and $E_p^{ox.}$ and $E_p^{red.}$ are peak potentials. [h] The oxidation of $Cp^*_2TiCl_2$ was reversible at 0 °C in methylene chloride ($E^{\circ\prime} = 1.25$ V) and at −40 °C in acetonitrile ($E^{\circ\prime} = 1.23$ V) but was irreversible at 22 °C in acetonitrile ($E_{1/2} = 1.22$ V). [i] Measured at −25 °C.

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(2) For a leading reference see: Maitlis, P. M. *Acc. Chem. Res.* **1978**, *11*, 301. Wolczanski, P. T.; Bercaw, J. E. *Ibid.* **1980**, *13*, 121. McLain, S. J.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5451. Manriquez, J. M.; Fagan, P. J.; Marks, T. J. *Ibid.* **1978**, *100*, 3939. Sikora, D. J.; Rausch, M. D.; Rogers, R. D.; Atwood, J. L. *Ibid.* **1981**, *103*, 1265. Freyberg, D. P.; Robbins, J. L.; Raymond, K. N.; Smart, J. C. *Ibid.* **1979**, *101*, 892. King, R. B. *Coord. Chem. Rev.* **1976**, *20*, 155.

(3) Thomas, J. L.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1386. Thomas, J. L. *Ibid.* **1973**, *95*, 1838. King, R. B.; Efraty, A. *Ibid.* **1972**, *94*, 3773.

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(6) For recent leading references to the use of electron spectroscopy for chemical analysis (ESCA)[6a–e] and ultraviolet photoelectron spectroscopy (UPS)[6b] in the characterization of transition-metal complexes see: (a) Lenhard, J. R.; Murray, R. W. *J. Am. Chem. Soc.* **1978**, *100*, 7870. Smith, D. F.; Willman, K.; Kuo, K.; Murray, R. W. *J. Electroanal. Chem.* **1979**, *95*, 217. Brant, P.; Benner, L. S.; Balch, A. L. *Inorg. Chem.* **1979**, *18*, 3422. Chatt, J.; Elson, C. M.; Leigh, G. J.; Connor, J. A. *J. Chem. Soc., Dalton Trans.* **1976**, 1351. Chatt, J.; Elson, C. M.; Hooper, N. E.; Leigh, G. J. *Ibid.* **1975**, 2392. Grim, S. O.; Matienzo, L. S. *Inorg. Chem.* **1975**, *14*, 1014. Xiang, S. F.; Chen, H. W.; Eyermann, C. J.; Jolly, W. L.; Smit, S. P.; Theopold, K. H.; Bergman, R. G.; Herrmann, W. A.; Pettit, R. *Organometallics* **1982**, *1*, 1200. (b) Calabro, D. C.; Hubbard, J. L.; Blevens, C. H., II; Campbell, A. C.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 6839. Calabro, D. C.; Lichtenberger, D. L. *Ibid.* **1981**, *103*, 6846. Calabro, D. C.; Lichtenberger, D. L.; Herrmann, W. A. *Ibid.* **1981**, *103*, 6852. Green, J. C.; Kelly, M. R.; Payne, M. P.; Seddon, E. A. Astruc, D.; Hamon, J.-R.; Michaud, P. *Organometallics* **1983**, *2*, 211. Condorelli, G.; Fragalà, I.; Centineo, A.; Tondello, E. *J. Organomet. Chem.* **1975**, *87*, 311. (c) Peterson, J. L.; Lichtenberger, D. L.; Fenske, R. F.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6433. (d) Cauletti, C.; Clark, J. P.; Green, J. C.; Jackson, S. E.; Fragala, I. L.; Ciliberto, E.; Coleman, A. W. *J. Electron Spectrosc. and Rel. Phenom.* **1980**, *18*, 61. Basso-Bert, M.; Cassoux, P.; Crasnier, F.; Gervais, D.; Labarre, J.-F.; DeLoth, P. *J. Organomet. Chem.* **1977**, *136*, 201. (e) Kadish, K. M.; Bottomely, L. A.; Brace, J. G.; Winograd, N. *J. Am. Chem. Soc.* **1980**, *102*, 4341. Demanet, C. M. *S. Afr. J. Chem.* **1982**, *35*, 45. Elson, C. M. *J. Chem. Soc., Dalton Trans.* **1975**, 2401.

(7) All ESCA spectra were measured on a Physical Electronics Industries, Inc., ESCA-Auger-SIMS system equipped with a Model 15-720 Specimen Introduction/Reaction Chamber, utilizing Mg Kα radiation. Samples were run on a polyethylene backing, and each sample was calibrated against the C(1s) binding energy (284.6 eV).[9] In this way, binding energies of ±0.1 eV could be routinely reproduced on various samples by different workers on different machines, since this calibration technique eliminated errors due to sample charging.

(8) Satisfactory elemental analysis and/or exact mass molecular weights were obtained on all new compounds.

(9) The C(1s) binding energy of polyethylene was referenced to a gold standard. "PHI Handbook of X-Ray Photoelectron Spectroscopy", Muilenberg, G. E., Ed.; Perkin-Elmer Corp.: Physical Electronics Division, Eden Prairie, MN, 1979. The width of the peaks measured at half-maximum was ≤1.7 eV. A mixture of Cp_2TiCl_2 and $Cp^*_2TiCl_2$ showed two resolved maxima at 457.1 and 456.2 eV for the Ti($2p_{3/2}$) peaks, respectively.

This concept was supported by comparison of $[CpFe(CO)_2]_2$ with $[Cp^*Fe(CO)_2]_2$ that showed a shift in binding energy of 0.4 eV on methyl substitution of the single Cp ligand.

For the series of compounds listed in Table I, average changes of 0.4 eV occurred for substitution of each C_5H_5 unit by a $C_5(CH_3)_5$ group. Feltham and Brant have noted that a one-electron oxidation of a transition metal results in a shift of approximately 1 eV to higher binding energy.[10] For the bis(cyclopentadienyl) complexes listed in Table I, we observed shifts of 0.8 eV (18.5 kcal/mol) on complete methyl substitution. Thus, *the substitution of two Cp* ligands for Cp ligands has an electronic effect approaching that of a one-electron reduction of the metal.*

Since the electrochemical oxidation of ferrocene to the ferrocenium ion has been thoroughly investigated,[11] it was of interest to compare the effect of methyl substitution on the ease of removing a valence electron from iron[12] vs. the ease of removal of an inner-shell electron. In general, this electrochemical data (Table I) supported our contention that methyl substitution on the cyclopentadienyl moiety has a dramatic electronic effect, which results in a systematic lowering of the $E^{\circ\prime}$ (or $E_{1/2}$). For the iron complexes listed in Table I, the substitution of five hydrogens by five methyl groups resulted in an average change of 0.3V in the $E^{\circ\prime}$ for the oxidation of iron. The titanocenes, zirconocenes, and hafnocenes presented a more difficult situation. Since the HOMO of these complexes cannot be associated with the metal atom,[6c,d] oxidation must involve one of the ligands. In contrast to the suggestion that titanocene dichloride has its HOMO associated with chloride,[6c] our electrochemical studies suggest that the HOMO is Cp based. The similarities in $E_{1/2}$ for the titanocene fluorides, chlorides, and bromides was diagnostic of oxidation of the Cp or Cp* moiety.[13,14]

In summary, we have shown that methyl substitution on the cyclopentadienyl group has a major influence on the electronic characteristics of metals that are complexed to this widely used ligand.

Acknowledgment. We are indebted to the National Science Foundation for a grant that partially supported this investigation.

Registry No. Cp_2TiF_2, 309-89-7; $CpCp^*TiF_2$, 38496-78-5; $Cp^*_2TiF_2$, 87050-22-4; Cp_2TiCl_2, 1271-19-8; $CpCp^*TiCl_2$, 38496-87-6; $Cp^*_2TiCl_2$, 11136-36-0; Cp_2TiBr_2, 1293-73-8; $CpCp^*TiBr_2$, 87050-23-5; Cp^*TiBr_2, 87050-24-6; Cp_2ZrCl_2, 1291-32-3; $CpCp^*ZrCl_2$, 81476-73-5; $Cp^*_2ZrCl_2$, 54039-38-2; Cp_2HfCl_2, 12116-66-4; $CpCp^*HfCl_2$, 87050-25-7; $Cp^*_2HfCl_2$, 85959-83-7; Cp_2Fe, 102-54-5; $CpCp^*Fe$, 83928-47-6; Cp^*_2Fe, 12126-50-0; $[CpFe(CO)_2]_2$, 12154-95-9; $[Cp^*Fe(CO)_2]_2$, 35344-11-7.

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[11] Slocum, D. W.; Ernst, C. R. *Adv. Organomet. Chem.* **1972**, *10*, 79. Kuwana, T.; Bublitz, D. E.; Hoh, G. *J. Am. Chem. Soc.* **1960**, *82*, 5811. Mason, J. G.; Rosenblum, M. *Ibid.* **1960**, *82*, 4206. Hoh, G. L. K.; McEwen, W. E.; Kleinberg, J. *Ibid.* **1961**, *83*, 3949. Little, W. F.; Eisenthal, R. *Ibid.* **1961**, *83*, 4936. Gubin, S. P.; Perevalova, E. G. *Dokl. Akad. Nauk SSSR* **1962**, *143*, 1351. Hall, D. W.; Russell, C. D. *J. Am. Chem. Soc.* **1967**, *89*, 2316. Sabattini, M. M.; Cesarotti, E. *Inorg. Chim. Acta* **1977**, *24*, L9. Grimes, H.; Logan, S. R.; *Ibid.* **1980**, *45*, L223. Deeming, A. J. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W.; Eds.; Pergamon Press: New York, **1982**; Vol. 4, p 480. Kotz, J. C.; Vining, W.; Coco, W.; Rosen, R.; Dias, A. R.; Garcia, M. H. *Organometallics* **1983**, *2*, 68.

[12] The oxidation of Cp^*_2Fe in molten $AlCl_3$/1-butylpyridinium chloride occurred 0.53 V more readily than the oxidation of Cp_2Fe. Gale, R. J.; Singh, P.; Job, R. *J. Organomet. Chem.* **1980**, *199*, C44. Their difference compares quite well with our difference of 0.54V measured in methylene chloride.

[13] This is consistent with recent studies of this system by Green and co-workers.[6d]

[14] The observation that the fluorides oxidized more easily than the corresponding chlorides or bromides was particularly interesting. We wish to speculate that in the titanocene difluorides the Cp (or Cp*) ligand is more ionic than in the analogous chlorides and bromides. As the ionic character of the Cp (or Cp*) ring increases, it becomes more easily oxidized to the corresponding radical. For comparison, we have shown that lithium pentamethylcyclopentadienide has an $E_{1/2}$ of −0.56 V and lithium cyclopentadienide[15] has an $E_{1/2}$ of −0.44 V in 90:10 THF–HMPA at −30 °C at a platinum electrode. The scan rate was 100 mV/s. This data supported our contention that the ease of oxidation of the cyclopentadienide system was a function of the ionic character of this species.

[15] For an earlier report of the $E_{1/2}$ of lithium cyclopentadienide ($E_{1/2}$ = −0.37 V) in 83:17 THF–HMPA at −60 °C at a carbon electrode see: Juan, B.; Schwarz, J.; Breslow, R. *J. Am. Chem. Soc.* **1980**, *102*, 5741.

Photochemically Induced Reductive Elimination of Ethane from a Binuclear Methylplatinum Complex[†]

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Summary: Photolysis (362 ± 7 nm) of $[Pt_2Me_3(\mu\text{-dppm})_2][PF_6]$, dppm = $Ph_2PCH_2PPh_2$, in pyridine leads to fragmentation to [PtMe$_2$(dppm)] and [PtMe(py)(dppm)]-[PF$_6$] (Φ = 0.6), but in MeCN (Φ = 0.1), acetone (Φ = 1.2 ± 0.3), or CH_2Cl_2 (Φ = 2.0 ± 0.1) photolysis gives a new reaction involving reductive elimination of ethane, followed by further reactions dependent on the solvent. Reductive elimination is at least partially intramolecular as shown by labeling studies.

There are reports of reductive elimination of H_2 from complexes $[L_nMH_2]$ and of CH_4 from $[L_nMMeH]$ using both thermal and photochemical activation[1,2] but, though thermal reductive elimination of ethane from $[L_nMMe_2]$ is well-known,[2] no similar photochemical reductive elimination involving C–C bond formation has been established.[1,3] We wish to report an example of this type of reaction involving a binuclear methylplatinum complex.

Photolysis of complexes I–III in pyridine or acetonitrile occurred according to eq 1,[6,7] and quantum yields (Table

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[†] Publication No. 298 from the photochemistry unit, University of Western Ontario

[1] Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry", Academic Press: New York, 1979.

[2] Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978.

[3] The closest analogy may be the coupling of aryl groups on photolysis of $[Ti(C_6H_4Me)_2(\eta\text{-}C_5H_5)_2]$,[4] but mechanistic studies have not been reported.[1] Several systems are known to give coupling of alkyl groups in low yield.[5]

[4] Erker, G. *J. Organomet. Chem.* **1977**, *134*, 189.

[5] Ozawa, F.; Yamamoto, A.; Ikariya, T.; Grubbs, R. H. *Organometallics* **1982**, *1*, 1481. Perkins, D. C. L.; Puddephatt, R. J.; Tipper, C. F. H. *J. Organomet. Chem.* **1979**, *166*, 261.

[6] Hill, R. H.; de Mayo, P.; Puddephatt, R. J. *Inorg. Chem.* **1982**, *21*, 3642. Geoffroy and co-workers report a quantum yield of 0.62 at 366 nm for photolysis of I in MeCN. Foley, H. C.; Morris, R. H.; Targos, T. S.; Geoffroy, G L. *J. Am. Chem. Soc.* **1981**, *103*, 7337.

[7] Brown, M. P.; Cooper, S. J.; Frew, A. A.; Manojlović-Muir, Lj.; Muir, K. W.; Puddephatt, R. J.; Thomson, M. A. *J. Chem. Soc., Dalton Trans.* **1982**, 299.

[8] Platinum-containing products were idetified by monitoring the course of photolysis by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy and were then isolated and characterized as described previously.[6,7,9] Volatile hydrocarbon products were determined by GC using 5A molecular sieve or Porapak Q columns and were within 20% of the values expected from the stoichiometry.

[9] Azam, K. A.; Puddephatt, R. J.; Brown, M. P.; Yavari, A. *J. Organomet. Chem.* **1982**, *234*, C31.

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