Organometallics **1982**, *1*, 1251–1254

reagent and allyl halides should be sufficient for the reaction, a little excess amount of halides is used for the sake of effective addition.

A typical experimental procedure is as follows. Lithium aluminum hydride (0.152 g, 4.0 mmol)[15] was added portionwise to a THF (10 mL) suspension of anhydrous manganese(II) chloride (0.50 g, 4.0 mmol) at 0 °C under an argon atmosphere. Spontaneous hydrogen evolution was observed, and a black fine suspension was produced. After the mixture was stirred at 0 °C for 30 min and at room temperature for 1 h, allyl bromide (0.174 mL, 2.0 mmol) dissolved in THF (5 mL) was added at room temperature, and the reaction mixture was stirred for 1.5 h. Benzaldehyde (0.143 mL, 1.41 mmol) in THF (5 mL) was then added to the reaction mixture, and the whole was stirred for 1.5 h at room temperature. Water (ca. 20 mL) was added, and the organic layer was extracted with ether. The ethereal layer was dried over anhydrous magnesium sulfate and concentrated. Chromatography of the residue on silica gel gave 1-phenyl-3-buten-1-ol (0.194 g, 93% yield).

Since chemoselective carbonyl addition is also observed for alkylmanganese iodides which are generated by metal exchange of alkyllithium with manganese(II) iodide,[16] C–C bond formation with manganese reagents will find expanding application. Synthetic studies dealing with low-valent manganese reagents are currently in progress in our laboratories.

Registry No. C_6H_5CHO, 75-07-0; *p*-$BuOC_6H_4CHO$, 5736-88-9; *p*-ClC_6H_4CHO, 104-88-1; *n*-$C_{10}H_{21}CHO$, 112-44-7; *i*-C_3H_7CHO, 78-84-2; *t*-C_4H_9CHO, 630-19-3; $C_6H_5CH(Me)CHO$, 93-53-8; C_6H_5COMe, 98-86-2; $C_6H_5CH{=}CHCHO$, 104-55-2; (*E*)-$CH_3CH{=}CHCHO$, 123-73-9; $C_6H_5CH(OH)CH_2CH{=}CH_2$, 936-58-3; *p*-$BuOC_6H_4CH(OH)CH_2CH{=}CH_2$, 82431-49-0; *p*-$ClC_6H_4CH(OH)CH_2CH{=}CH_2$, 14506-33-3; *n*-$C_{10}H_{21}CH(OH)CH_2CH{=}CH_2$, 26496-21-9; *i*-$C_3H_7CH(OH)CH_2CH{=}CH_2$, 32815-70-6; *t*-$C_4H_9CH(OH)CH_2CH{=}CH_2$, 19550-89-1; $C_6H_5CH(Me)CH(OH)CH_2CH{=}CH_2$ Isomer I, 80410-52-2; $C_6H_5CH(Me)CH(OH)CH_2CH{=}CH_2$ Isomer II, 80401-09-8; $C_6H_5C(OH)(Me)CH_2CH{=}CH_2$, 4743-74-2; $C_6H_5CH{=}CHCH(OH)CH_2CH{=}CH_2$, 13891-95-7; (*E*)-$CH_3CH{=}CH{-}CH(OH)CH_2CH{=}CH_2$, 24581-03-1; $C_6H_5CH(OH)CH(Me)CH{=}CH_2$ Isomer I, 52922-19-7; $C_6H_5CH(OH)CH(Me)CH{=}CH_2$ Isomer II, 52922-10-8; *n*-$C_{10}H_{21}CH(OH)CH(Me)CH{=}CH_2$ Isomer I, 82431-51-4; *n*-$C_{10}H_{21}CH(OH)CH(Me)CH{=}CH_2$ Isomer II, 82431-52-5; *i*-$C_3H_7CH(OH)CH(Me)CH{=}CH_2$ Isomer I, 1502-90-5; *i*-$C_3H_7CH(OH)CH(Me)CH{=}CH_2$ Isomer II, 1502-91-6; *t*-$C_4H_9CH(OH)CH(Me)CH{=}CH_2$ Isomer I, 1502-89-2; *t*-$C_4H_9CH(OH)CH(Me)CH{=}CH_2$ Isomer II, 1502-88-1; $CH_3CH{=}CHCH(OH)CH(Me)CH{=}CH_2$ (*E*) Isomer I, 82468-21-1; $CH_3CH{=}CHCH(OH)CH(Me)CH{=}CH_2$ (*E*)-Isomer II, 82468-22-2; $C_6H_5CH(OH)C(Me)_2CH{=}CH_2$, 27644-02-6; $C_6H_5CH(OH)CH_2CH{=}CH_2$, 936-58-3; cyclohexanone, 108-94-1; 5-isopropenyl-2-methyl-2-cyclohexenone, 99-49-0; *p-tert*-butylcyclohexanone, 98-53-3; 1-(2-propenyl)cyclohexanol, 1123-34-8; 5-isopropenyl-2-methyl-1-(2-propenyl)-2-cyclohexenol, 82431-50-3; *cis-p-tert*-butyl-1-(1-methyl-2-propenyl)cyclohexanol, 75735-19-5; *trans-p-tert*-butyl-1-(1-methyl-2-propenyl)cyclohexanol), 75735-06-7; *cis-p-tert*-butyl-1-(2-propenyl)cyclohexanol, 42437-24-1; *trans-p-tert*-butyl-1-(2-propenyl)cyclohexanol, 42437-23-0; allyl bromide, 106-95-6; crotyl bromide, 4784-77-4; prenyl bromide, 870-63-3; allyl diethyl phosphate, 3066-75-9; allyl chloride, 107-05-1; manganese(II) chloride, 7773-01-5; manganese, 7439-96-5.

---

(13) The stereochemistry in the nucleophilic addition to cyclohexanones has been discussed by Cieplak recently. According to his theory, the crotyl anion is softer than the allyl anion, and therefore equatorial attack is preferred in the crotyl addition. Cieplak, A. S. *J. Am. Chem. Soc.* **1981**, *103*, 4540–4552. See also: Gaudemar, M. *Tetrahedron* **1976**, *32*, 1689–1691.

(14) Kimura, K.; Takai, K.; Nozaki, H. The 45th National Annual Meeting of Chemical Society of Japan, 3C38, Tokyo, 1982.

(15) Purchased from A. G. Metalgeselschaft West Germany.

(16) Cahiez, G.; Normant, J. F. *Tetrahedron Lett.* **1977**, 3383–3384; *Bull. Soc. Chim. Fr.* **1977**, 570. Cahiez, G.; Bernard, D.; Normant, J. F. *Synthesis* **1977**, 130–133. Cahiez, G. *Tetrahedron Lett.* **1981**, *22*, 1239.

Catalysis by Solvated Transition-Metal Cations. 3.[1] Novel Catalytic Transformations of Alkenes by Cationic Compounds of Molybdenum and Tungsten

Ayusman Sen* and Richard R. Thomas

Chandlee Laboratory, Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802

Received January 28, 1982

Summary: The compounds $[M(NO)_2(CH_3CN)_4](BF_4)_2$; (**2**, M = Mo; **3**, M = W) were synthesized through reactions of the corresponding metal hexacarbonyls with 2 equiv of $NOBF_4$ in acetonitrile. These compounds catalyze the polymerization, oligomerization, and rearrangement of olefins.

In previous communications,[1] we had demonstrated, using $[Pd(CH_3CN)_4](BF_4)_2$, **1**, as an example, that incipient carbonium ions may be generated by the interaction of olefins with electrophilic transition-metal centers and that such species may play an important role in transition-metal-catalyzed oligomerization, polymerization, and rearrangement of olefins. We now show, using cationic compounds of molybdenum and tungsten as examples, that the above-mentioned process is indeed quite general and with small variations is also observed for "early" transitional elements.

The compounds *cis*-$[Mo(NO)_2(CH_3CN)_4](BF_4)_2$,[2a] **2**, and *cis*-$[W(NO)_2(CH_3CN)_4](BF_4)_2$,[2b] **3**, were synthesized through the reactions of the corresponding metal hexacarbonyls with 2 equiv of $NOBF_4$ in acetonitrile (eq 1).

$$M(CO)_6 + 2NOBF_4 \xrightarrow[25\ °C]{CH_3CN} [M(NO)_2(CH_3CN)_4](BF_4)_2 + 6\,CO \quad (1)$$
$$\mathbf{2},\ M = Mo \qquad \mathbf{3},\ M = W$$

Following precipitation by diethyl ether, dark green hygroscopic solids were isolated. The ^1H NMR spectra (in CD_3NO_2) of both **2** and **3** exhibited two absorptions of equal intensity at 2.65 and 2.55 ppm, respectively, which is an indication of cis configuration of NO groups around the metals. In CD_3CN, for freshly prepared solutions of both **2** and **3**, only one peak at 2.55 ppm is visible together with a peak at 1.95 ppm corresponding to uncomplexed CH_3CN, perhaps indicating the greater lability of two of the four bound CH_3CN molecules. Furthermore, when the solutions were left standing for several hours at room temperature, the peak at 2.55 ppm for both **2** and **3** disappears completely together with an increase in intensity of the peak at 1.95 ppm. Thus all four CH_3CN molecules in **2** and **3** are labile and exchange with free CH_3CN molecules (eq 2).

$$\underset{\mathbf{2},\ M = Mo;\ \mathbf{3},\ M = W}{M(NO)_2(CH_3CN)_4^{2+}} + 4CD_3CN \xrightarrow[25\ °C]{} M(NO)_2(CD_3CN)_4^{2+} + 4CH_3CN \quad (2)$$

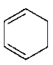
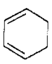
---

(1) For previous parts in this series, see: (a) Sen, A.; Lai, T.-W. *J. Am. Chem. Soc.* **1981**, *103*, 4627. (b) *Organometallics* **1982**, *1*, 415.

(2) (a) $[Mo(NO)_2(CH_3CN)_4](BF_4)_2$, **2**: IR (Nujol) $\bar{\nu}(C{\equiv}N)$ 2360, 2310 cm^{-1}, $\bar{\nu}(NO)$ 1860, 1760, 1730 cm^{-1}, $\bar{\nu}(BF_4^-)$ 1200–1000 cm^{-1}. Anal. Calcd for $MoC_8H_{12}N_6O_2B_2F_8$: C, 19.5; H, 2.5. Found: C, 19.0; H, 2.4. (b) $[W(NO)_2(CH_3CN)_4](BF_4)_2$, **3**: IR (Nujol) $\bar{\nu}(C{\equiv}N)$ 2330, 2300 cm^{-1}; $\bar{\nu}(NO)$ 1860, 1820, 1770, 1730 cm^{-1}; $\bar{\nu}(BF_4^-)$ 1200–1000 cm^{-1}; conductivity (CH_3CN) slope ($\Lambda_o - \Lambda_e$ vs. $C^{1/2}$) = 355. Anal. Calcd for $WC_8H_{12}N_6O_2B_2F_8$: C, 16.4; H, 2.1. Found: C, 16.7; H, 2.1.

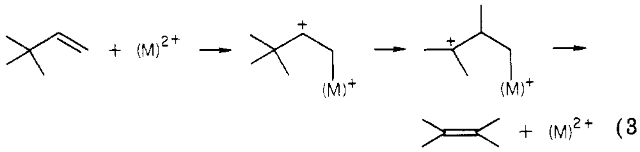
0276-7333/82/2301-1251$01.25/0

Table I. Catalytic Polymerization of Olefins by $[M(NO)_2(CH_3CN)_4](BF_4)_2$ (M = Mo, W)[a]

catalyst	monomer	monomer/ catalyst	temp, °C	time	yield,[b] %	product	$\overline{M}_n$[c]
$Mo(NO)_2(CH_3CN)_4^{2+}$	CH_2=CHPh	250	25	4 h	>95	polymer	36000
$Mo(NO)_2(CH_3CN)_4^{2+}$	CH_2=C(Me)Ph	100	25	1 h	>95	oligomers	
$Mo(NO)_2(CH_3CN)_4^{2+}$	CH_2=C(Me)Ph	200	0	2 h	>95	polymer	7000
$Mo(NO)_2(CH_3CN)_4^{2+}$		100	25	1 day	>95	polymer	600
$Mo(NO)_2(CH_3CN)_4^{2+}$		100	25	1 day	>95	polymer	d
$W(NO)_2(CH_3CN)_4^{2+}$	CH_2=CHPh	250	25	4 h	85	polymer	42000
$W(NO)_2(CH_3CN)_4^{2+}$	CH_2=C(Me)Ph	200	25	1 h	>95	oligomers	
$W(NO)_2(CH_3CN)_4^{2+}$	CH_2=C(Me)Ph	200	0	6 h	>95	polymer	8500
$W(NO)_2(CH_3CN)_4^{2+}$	CH_2=C(Me)Ph	200	−23	6 h	85	polymer	36000
$W(NO)_2(CH_3CN)_4^{2+}$		100	25	1 day	65	polymer	3200

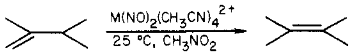
[a] CH_3NO_2 was used as solvent. The reactions were performed in an inert atmosphere glovebox. [b] Yields reported are those of isolated pure materials. [c] Molecular weights of polymers were determined by gel permeation chromatography using solutions of polymers in tetrahydrofuran. The weights reported are those of standard polystyrene samples having gpc traces similar to those observed. [d] The polymer was insoluble in all common organic solvents.

A test of the ability of **2** and **3** to generate incipient carbonium ions by interaction with olefins involved the reaction of *tert*-butylethylene with these two compounds. Indeed, like **1**,[1a] **2** and **3** were also found to catalyze the skeletal rearrangement of *tert*-butylethylene to tetramethylethylene at room temperature in CH_3NO_2 (eq 3).



(3)

In addition, **2** and **3** were also found to catalyze the C=C bond migration in olefins, e.g., eq 4.

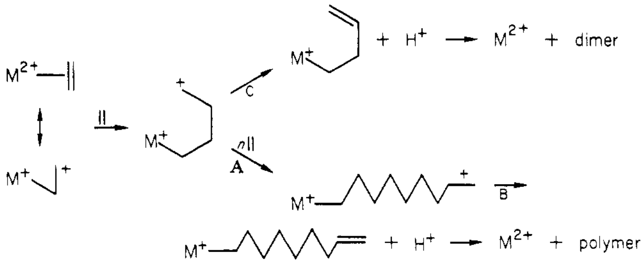


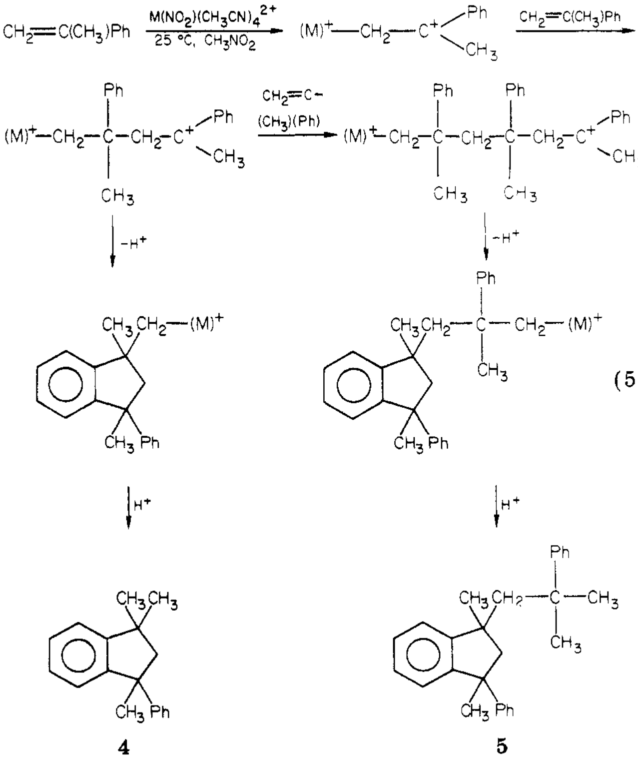
(4)

M = Mo, W

If incipient carbonium ions are generated by the reaction of **2** or **3** with olefins, then **2** and **3** should act as good initiators for the cationic polymerization of olefins. In fact, this has been observed and the results are summarized in Table I. We had earlier proposed,[1a] the following schematic mechanism for the oligomerization and polymerization of olefins by electrophilic transition-metal cations (Scheme I). According to this mechanism, the chain length of the polymer would depend on the relative rates of chain propogation (step A) and chain termination by loss of H^+ (step B or C). If step A is significantly slower than step C, only dimers would be obtained. Furthermore, if the activation energy for chain termination is greater than that for chain propogation, then the molecular weight would be expected to increase as the reaction temperature is lowered,[3] and we find this to be true for the polymerization of α-methylstyrene by either **2** or **3** (Table I). At room temperature, only a mixture of head-to-tail cyclic dimer (**4**)[5a] and trimer (**5**)[5b] were formed (eq 5). Using substrate/catalyst ratio of 100/1, ~1/3 mixture of **4** and **5** was obtained with **2** (90% yield in 1 h) and ~1/2 mixture of **4** and **5** was obtained with **3** (76% yield in 1 h).

Scheme I





(5)

4

5

M = Mo, W

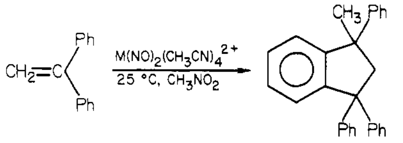
---

[3] This is one of the characteristic features of cationic polymerization processes.[4]

[4] Allcock, H. R.; Lampe, F. W. "Contemporary Polymer Chemistry"; Prentice-Hall: New Jersey, 1981; Chapter 4.

[5] (a) ^{1}H NMR ($CDCl_3$): 7.4–7.0 (9 H, Ph), 2.45, 2.18 (2 H, ABq, *J* = 12.8 Hz, CH_2), 1.69, 1.32, 1.03 ppm (9 H, CH_3). ^{13}C NMR {^{1}H} ($CDCl_3$): 150.9–148.7, 127.9–122.5, 59.4, 50.8, 42.8, 30.8, 30.4 ppm. Mass spectrum, *m/e* 236 (M^+), 221 (M − 15). (b) ^{1}H NMR ($CDCl_3$): 7.4–7.0 (14 H, Ph), 2.59, 1.92 (2 H, ABq, *J* = 13.4 Hz, CH_2), 2.16, 1.70 (2 H, ABq, *J* = 14.6 Hz, CH_2); 1.61, 1.28, 1.14, 0.95 ppm (12 H, CH_3). ^{13}C NMR {^{1}H} ($CDCl_3$): 153.7–148.3, 127.9–122.9, 57.4, 54.9, 51.2, 47.6, 38.6, 33.4, 30.8, 29.2, 28.6 ppm. Mass spectrum *m/e* 339 (M − 15).

The head-to-tail cyclic dimer 1,1,3-triphenyl-3-methylindan[6] was the sole product in the catalytic dimerization of 1,1-diphenylethylene by either **2** or **3** at room temperature (eq 6).

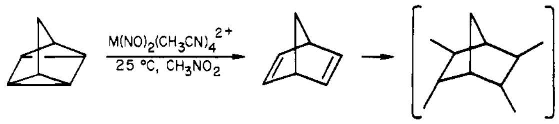


(6)

M = Mo, W

The ^{1}H NMR spectra of poly(1,3-cyclohexadiene) obtained by using either **2** or **3** as catalyst exhibit three broad resonances at 5.8 (H_o), 2.0 (H_α), and 1.6 ppm (H_β), the first two representing respectively the vinylic and allylic protons present in the polymer. Two possible types of polymers (1,2 and 1,4) may arise through the cationic polymerization of 1,3-cyclohexadiene,[7] and these, together with their expected ^{1}H NMR data, are shown in Table II.[7a] The ratio, H_α/H_β, in the polymer obtained by using **3** as catalyst is ~0.6, thus indicating that it is a mixture of 1,2- and 1,4-poly(1,3-cyclohexadiene), with the latter predominating. The ratio, $H_o/(H_\alpha + H_\beta)$, is a measure of the degree of branching or cross-linking that is present in the polymer ($H_o/(H_\alpha + H_\beta) = 0.33$ for unbranched polymers and 0 for completely cross-linked polymer). In the present case, $H_o/(H_\alpha + H_\beta) = 0.30$, thus indicating the presence of only a very modest degree of cross-linking. The poly(1,3-cyclohexadiene) obtained by using **2** as catalyst exhibits structural features similar to the polymer described above.

The poly(norbornadiene) obtained through the reaction of norbornadiene with either **2** or **3** appears to be virtually insoluble in all common organic solvents, a feature indicative of the presence of extensive cross-linking.[8] The same polymer was also obtained starting with quadricyclane, which was converted to norbornadiene within seconds, the latter, if left in the reaction mixture, being then slowly polymerized (eq 7).

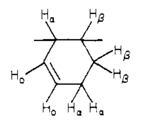
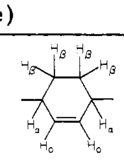


(7)

M = Mo, W

It is important to distinguish between the chemistry described above from that observed with H^+ as catalyst, since the latter could, in principle, form through the interaction of the electrophilic metal centers with either the solvent or protic impurities. An important distinction between the chemistry that we have observed for electrophilic CH_3CN-coordinated transition-metal cations such as **1**, **2**, and **3** on one hand and $HBF_4{\cdot}Et_2O$ on the other is that unlike the latter species; the former compounds were all significantly less reactive in CH_3CN than in CH_3NO_2. For example, while $HBF_4{\cdot}Et_2O$ would initiate the rapid polymerization of styrene at 25 °C in CH_3CN, **2** and **3** were virtually inactive in this solvent. We ascribe this to the failure of the olefin to compete successfully with CH_3CN for the coordination sphere of the metal, when the latter is used as the solvent, and would appear to indicate a direct participation of the metal in the polymerization process. In fact, there exists a marked gradation in the catalytic activity of the CH_3CN-coordinated transition-metal cations as a function of the solvent. For example, $Pd(CH_3CN)_4^{2+}$ initiated rapid polymerization of styrene in both CH_3CN and CH_3NO_2,[1b] while $M(NO)_2(CH_3CN)_4^{2+}$ (M = Mo, W) initiated this polymerization only in CH_3NO_2. On the other hand, $M(CH_3CN)_6^{2+}$ (M = Co, Ni) did not polymerize styrene in CH_3CN and did so extremely slowly (days vs. hours for **2** and **3**) in CH_3NO_2. This gradation in catalytic activity appears to be a direct function of the substitutional lability of the coordinated CH_3CN ligands. Indeed it is remarkable that compounds of the type $M(CH_3CN)_x(PPh_3)_y^{2+}$ (M = Ni, Co) were converted quantitatively to $M(CH_3CN)_6^{2+}$ on dissolution in CH_3CN. The following observations also serve to distinguish between the chemistry observed with **2** and **3** on one hand and $HBF_4{\cdot}Et_2O$ on the other. The polystyrene obtained by using **3** as catalyst has a slight syndiotacticity, whereas that obtained through the use of $HBF_4{\cdot}Et_2O$ is random. The predominant product in the room temperature oligomerization of α-methylstyrene by **2** and **3** was the cyclic trimer, **5** (vide supra), whereas the cyclic dimer **4** predominates (>80%) under the same condition when $HBF_4{\cdot}Et_2O$ is used as catalyst. Finally, the sequence of reactions depicted in eq 7 took place in CH_3CN (albeit more slowly than in CH_3NO_2) by using **3** as catalyst, whereas $HBF_4{\cdot}Et_2O$ was virtually inactive.

Table II. Expected ^{1}H NMR Data for Poly(1,3-cyclohexadiene)

	 1,2-poly-(cyclohexadiene)	 1,4-poly-(cyclohexadiene)
$H_o/(H_\alpha + H_\beta)$	1/3	1/3
H_α/H_β	1/1	1/2

In conclusion, it appears that the generation of incipient carbonium ions by the interaction of olefins with electrophilic transition-metal compounds is a general phenomenon. Indeed a similar reactivity pattern has been observed for the weakly ligated transition-metal cations $[Pt(CH_3CN)_4](BF_4)_2$,[9] $[Rh(NO)(CH_3CN)_4](BF_4)_2$,[10] and $[Fe(NO)_2(solv)_n]X$,[11] (solv = CH_2Cl_2, THF, CH_3CN; X = PF_6, BF_4, ClO_4), and these reactions may well follow the same mechanistic pathway. Finally, our postulate concerning the formation of incipient carbonium ions through the interaction of olefins with electrophilic transition-metal centers has recently received support on theoretical grounds.[12] Furthermore, the crystal structures of several metal complexes containing monosubstituted olefins containing electron-donating substituents show,[13] as expected, that the metal–carbon distance to the unsubstituted carbon is significantly shorter than that to the substituted carbon, since the incipient carbonium ion would be located on the carbon bearing the electron-donating substituent. This carbon is also the preferred site of attack by nucleophiles.[13]

---

(6) ^{1}H NMR ($CDCl_3$): 7.4–7.0 (19 H, Ph), 3.45, 3.10 (2 H, ABq, *J* = 12 Hz, CH_2); 1.6 ppm (3 H, CH_3). ^{13}C NMR {^{1}H} ($CDCl_3$): 150.5–147.5, 128.8–125.0, 61.4, 60.9, 51.2, 28.9 ppm. Mass spectrum *m/e* 360 (M^+), 283 (M – 77).

(7) (a) Imanishi, Y.; Matsuzaki, K.; Yamane, T.; Kohjiya, S.; Okamura, S. *J. Macromol. Sci., Chem.* **1969**, *A3*, 249. (b) Kennedy, J. P. "Cationic Polymerization of Olefins: A Critical Inventory"; Wiley Interscience: New York, 1975; p 192.

(8) Reference 7b, p 223.

(9) de Renzi, A.; Panunzi, A.; Vitagliano, A.; Paiaro, G. *J. Chem. Soc., Chem. Commun.* **1976**, 47.

(10) Connelly, N. G.; Draggett, P. T.; Green, M. *J. Organomet. Chem.* **1977**, *140*, C10.

(11) Ballivet-Tkatchenko, D.; Billard, C.; Revillon, A. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 1697.

(12) Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4308.

(13) Chang, T. C. T.; Foxman, B. M.; Rosenblum, M.; Stockman, C. *J. Am. Chem. Soc.* **1981**, *103*, 7361.

Acknowledgment. Financial support of this research through grants from the Department of Energy, Office of Basic Energy Sciences, and by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Registry No. 2, 82583-10-6; **3**, 82583-08-2; **4**, 3910-35-8; **5**, 41906-71-2; $W(CO)_6$, 14040-11-0; $Mo(CO)_6$, 13939-06-5; *tert*-butylethylene, 558-37-2; tetramethylethylene, 563-79-1; 1,1-diphenylethylene, 530-48-3; poly(1,3-cyclohexadiene), 27986-50-1; poly(norbornadiene), 27859-77-4; quadricyclane, 278-06-8; norbornadiene, 121-46-0; polystyrene, 9003-53-6; poly(2-methylstyrene), 25014-31-7; 1,1,3-triphenyl-3-methylindan, 19303-32-3.

Structure and Bonding in a Phosphenium Ion–Iron Complex, $Fe[\eta^5\text{-}(CH_3)_5C_5](CO)_2[PN(CH_3)CH_2CH_2NCH_3]$. A Demonstration of Phosphenium Ion Acceptor Properties

Larry D. Hutchins, Eileen N. Duesler, and Robert T. Paine*

Department of Chemistry, University of New Mexico
Albuquerque, New Mexico 87131

Received July 2, 1982

Summary: The combination of $NaFe[\eta^5\text{-}(CH_3)_5C_5](CO)_2$ with $CH_3NCH_2CH_2N(CH_3)PF$ in THF results in the formation of a metallophosphenium ion complex $Fe[\eta^5\text{-}(CH_3)_5C_5](CO)_2[PN(CH_3)CH_2CH_2NCH_3]$. The air-sensitive compound has been characterized by IR and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopies and single-crystal X-ray crystallography. The molecular structure contains a relatively long Fe–P bond distance, 2.340 (2) Å, and unlike other monometallic phosphenium ion complexes the geometry about the phosphorus atom is pyramidal instead of planar. The molecular structure is consistent with the cyclic phosphenium ion acting as an electron acceptor toward the electron-saturated $Fe[\eta^5\text{-}(CH_3)_5C_5](CO)_2^-$ fragment.

The interaction of selected aminohalophosphines with metal carbonyl anions leads to the heterolytic cleavage of the phosphorus–halogen bond and the formation of metallophosphenium ion complexes.[1-3] Molecular structure determinations for two compounds, $Mo(\eta^5\text{-}C_5H_5)(CO)_2[PN(CH_3)CH_2CH_2NCH_3]$ (**1**) and $Co_2(CO)_5[PN(CH_3)CH_2CH_2NCH_3]_2$ (**2**), have revealed that the cyclic phosphenium ion, $[PN(CH_3)CH_2CH_2NCH_3^+]$, may act as a terminal or bridging ligand,[2,3] and chemical properties and bonding analyses have suggested that $(R_2N)_2P^+$ species have both σ-donor and π-acceptor functionality.[2-6] In addition, intriguing similarities between phosphenium ions and carbenes,[7] SO_2,[8] and NO[9] have now become apparent. In this regard, we have briefly reported on the synthesis of a phosphenium ion–iron complex, $Fe(\eta^5\text{-}C_5H_5)(CO)_2[PN(CH_3)CH_2CH_2NCH_3]$ (**3**) from the combination of $NaFe(\eta^5\text{-}C_5H_5)(CO)_2$ and $CH_3NCH_2CH_2N(CH_3)PF$.[1] However, attempts to fully characterize **3** have been frustrated by decomposition reactions. We now wish to report the synthesis, characterization and crystal structure determination for the related complex $Fe[\eta^5\text{-}(CH_3)_5C_5](CO)_2[PN(CH_3)CH_2CH_2NCH_3]$ (**4**).[10]

Compound **4** was prepared by combination of $CH_3NCH_2CH_2N(CH_3)PF$[11] with an equimolar amount of $NaFeCp^*(CO)_2$[12,13] in tetrahydrofuran (THF). No CO was evolved, and a red, crystalline, air-sensitive solid was obtained.[15] The course of the reaction is summarized by eq 1. The absence of CO evolution suggests that the nature

$$\mathrm{CH_3NCH_2CH_2N(CH_3)PF + NaFeCp^*(CO)_2} \xrightarrow[25\ ^\circ\mathrm{C}]{\mathrm{THF}} \mathrm{NaF} + \underset{\mathbf{4}}{\mathrm{CH_3NCH_2CH_2N(CH_3)PFeCp^*(CO)_2}} \quad (1)$$

of the phosphenium ion interaction with the $FeCp^*(CO)_2^-$ fragment is uniquely different from the metal–phosphenium ion interactions in **1** and **2**.

The compound was initially characterized by elemental analysis and infrared and NMR spectroscopies.[15] A com-

---

[1] Light, R. W.; Paine, R. T. *J. Am. Chem. Soc.* **1978**, *100*, 2230.

[2] Hutchins, L. D.; Paine, R. T.; Campana, C. F. *J. Am. Chem. Soc.* **1980**, *102*, 4521.

[3] Hutchins, L. D.; Light, R. W.; Paine, R. T. *Inorg. Chem.* **1982**, *21*, 266.

[4] Thomas, M. G.; Kopp, R. W.; Schultz, C. W.; Parry, R. W. *J. Am. Chem. Soc.* **1974**, 96, 2646. Thomas, M. G.; Schultz, C. W.; Parry, R. W. *Inorg. Chem.* **1977**, *16*, 994.

[5] Montemayor, R. G.; Sauer, D. T.; Fleming, S.; Bennett, D. W.; Thomas, M. G.; Parry, R. W. *J. Am. Chem. Soc.* **1978**, *100*, 2231. Bennett, D. W.; Parry, R. W. *Ibid.* **1979**, *101*, 755.

[6] Cowley, A. H.; Kemp, R. A.; Wilburn, J. C. *Inorg. Chem.* **1981**, *20*, 4289. Cowley, A. H.; Cushner, M. C.; Szobota, J. S. *J. Am. Chem. Soc.* **1978**, *100*, 7784. Baxter, S. G.; Collins, R. L.; Cowley, A. H.; Sena, S. F. *Ibid.* **1981**, *103*, 714. Cowley, A. H.; Cushner, M. C.; Lattman, M.; McKee, M. L.; Szobota, J. S.; Wilburn, J. C. *Pure Appl. Chem.* **1980**, *52*, 789.

[7] The chemistry, structures, and bonding in metal carbene complexes have been described in several recent reviews: Cardin, D. J.; Cetinkaya, B.; Lappert, M. F. *Chem. Rev.* **1972**, *72*, 545. Cotton, F. A.; Lukehart, C. M. *Prog. Inorg. Chem.* **1972**, *16*, 487. Brown, F. J. *Prog. Inorg. Chem.* **1980**, *27*, 1. Fischer, E. O. *Adv. Organomet. Chem.* **1976**, *14*, 1.

[8] The structures and bonding in metal–SO_2 complexes have been recently reviewed: Ryan, R. R.; Kubas, G. J.; Moody, D. C.; Eller, P. G. *Struct. Bonding* (*Berlin*) **1981**, *46*, 47.

[9] The structures and bonding in metal-nitrosyl complexes have been reviewed: Enemark, J. H.; Feltham, R. D. *Coord. Chem. Rev.* **1974**, *13*, 339. Eisenberg, R.; Meyer, C. D. *Acc. Chem. Res.* **1975**, *8*, 26.

[10] Several reports of $CpFe(CO)_2(carbene)^+$ complexes have appeared, and representative examples are described in the following references: Fischer, E. O.; Kreis, G.; Kreissel, F. R.; Kreiter, C. G.; Muller, J. *Chem. Ber.* **1973**, *106*, 3910. McCormick, F. B.; Angelici, R. J. *Inorg. Chem.* **1979**, *18*, 1231. McCormick, F. B.; Angelici, R. J. *Ibid.* **1981**, *20*, 1111 and additional references can be found in ref 7. The formation of monometallic $FeCp(CO)_2SO_2^{0/+1}$ compounds has not been reported; however, bimetallic complexes $[FeCp(CO)_2]_2SO_2$ and $[FeCp(CO)]_2(CO)(SO_2)$ have been described: Churchill, M. R.; DeBoer, B. G.; Kalra, K. L. *Inorg. Chem.* **1973**, *12*, 1649. Churchill, M. R.; Kalra, K. L. *Ibid.* 1650.

[11] Fleming, S.; Lupton, M. K.; Jekot, K. *Inorg. Chem.* **1972**, *11*, 2534.

[12] Abbreviations used in the text include tetrahydrofuran, THF and pentamethylcyclopentadienide, Cp*.

[13] $NaFeCp^*(CO)_2$ was prepared by Na/Hg amalgam reduction of $[FeCp^*(CO)_2]_2$[14] in THF solution.

[14] King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1967**, *8*, 287.

[15] Compound **4** was isolated under inert-atmosphere conditions by filtration of the reaction mixture followed by vacuum evaporation of the THF filtrate. The evaporate was extracted with benzene and filtered, and a red solid (**4**) was recovered by vacuum evaporation of the benzene filtrate. The yield was 90%. Sublimation (65 °C (10^{-3} torr)) resulted in the recovery of pure, crystalline product: IR (carbonyl region, Nujol) 2002 (m), 1969 (s), 1954 (s), 1914 (s) cm^{-1}; NMR (32 °C, benzene) ^1H δ 3.07 (m, phosphenium ion methylene), 2.63 (d, $^3J_{HCNP} = 13.3$ Hz, phosphenium ion methyl), 1.67 (Cp* methyl), $^{13}C\{^1H\}$, δ 217.9 (d, $^2J_{CFeP} = 3.0$ Hz, carbonyls), 95.89 (Cp* ring), 54.78 (d, $^2J_{CNP} = 10.1$ Hz, phosphenium ion methylene), 35.23 (d, $^2J_{CNP} = 21.3$ Hz, phosphenium ion methyl), 9.31 ($^3J_{CCFeP} = 10.3$ Hz, Cp* methyl), $^{31}P\{^1H\}$ (85% H_3PO_4 standard), δ 285.9 (phosphenium ion phosphorus). Anal. Calcd for $FePO_2N_2C_{16}H_{25}$: Fe 15.3; P, 8.5; O, 8.8; N, 7.7; C, 52.8; H, 6.9. Found: Fe, 14.7; P, 8.1; O, 10.8; N, 7.5; C, 51.6; H, 6.8.