In view of the chemistry just presented in eqs 2-7, these aluminate adducts could form by proton abstraction and nucleophilic attack through a four-centered transition state. It is, of course, also possible that these processes occur by stepwise, noncyclic pathways. Finally, both OCS and CS_2 react with 1 to give $[(CH_3)_2AlS]^-$. The reactions with OCS and CS_2 are similar to those between these neutral species and $[(CH_3)_3SiO]^-$.[11,12]

Additional studies of 1 and related ions are in progress.

Acknowledgment. We thank the National Science Foundation (Grant Nos. CHE-8615808 and 8921522) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. We are also grateful to Band Gap Technologies for the gift of a sample of trimethylaluminum.

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[11] O'Hair, R. A. J.; Sheldon, J. C.; Bowie, J. H.; Damrauer, R.; DePuy, C. H. *Aust. J. Chem.* **1989**, *42*, 489.

[12] The reaction rates of 1 and $[(CH_3)_3SiO]^-$ with CS_2 are 5.8×10^{-10} and 1.4×10^{-10} cm^3 (molecule)$^{-1}$ s^{-1}, respectively; with OCS the rates are 9.6×10^{-10} and 6.5×10^{-10} cm^3 (molecule)$^{-1}$ s^{-1}, respectively. The corresponding reaction efficiencies are 0.53, 0.13, 0.88, and 0.62.

Lithium-Tellurium Exchange Reaction. A Convenient Method for Generation of Heteroatom-Substituted Methyllithiums

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Summary: A variety of heteroatom-substituted methyllithiums (GCH_2Li; G = $MeOCH_2CH_2O-$, $PhCH_2O-$, Me_2N-, Me_3Si-, Me_3Ge-, $^nBu_3Sn-$, $^nBuTe-$) were generated by the lithium-tellurium exchange reaction of corresponding tellurides with butyllithium and were trapped with electrophiles. The potent utility of bis(butyltelluro)methane as a methylene dianion synthon was demonstrated, where both of the butyltelluro groups were displaced stepwise by different electrophiles with use of this metalation/trapping sequence repeated twice.

Heteroatom-substituted organolithium compounds[1] are very useful reagents for construction of carbon skeletons with coincidental introduction of functional groups. As for the generation of these organolithiums, a lithium-tin exchange reaction has been frequently employed when a conventional hydrogen abstraction or lithium-halogen exchange reaction cannot be applied. Recently, we have demonstrated that diorganyl tellurides undergo rapid transmetalation by the reaction with alkyllithiums to give thermodynamically more stable organolithium compounds.[2] These successful results led us to attempt the formation of heteroatom-substituted methyllithiums **2** such as (alkoxymethyl)-,[3] (aminomethyl)-,[4] (silylmethyl)-,[5] (germylmethyl)-,[6] (stannylmethyl)-,[7] and (telluromethyl)lithiums[8] via lithium-tellurium exchange reactions.

$$\underset{\mathbf{1}}{GCH_2\text{-}Te^nBu} \xrightarrow[-^nBu_2Te]{^nBuLi} \underset{\mathbf{2}}{[GCH_2\text{-}Li]} \xrightarrow{\text{electrophile}} \text{product} \qquad (1)$$

a, G = OCH_2CH_2OMe; **b**, G = OCH_2Ph; **c**, G = NMe_2; **d**, G = $SiMe_3$; **e**, G = Te^nBu; **f**, G = Sn^nBu_3

When butyllithium was added to the THF solution of butyl (2-methoxyethoxy)methyl telluride (**1a**)[9] at -78 °C, lithium-tellurium exchange proceeded efficiently to give the corresponding (alkoxymethyl)lithium **2a**. Addition of benzaldehyde to the resulting mixture followed by the usual workup gave the β-alkoxy alcohol **3** in 70% yield together with 76% of dibutyl telluride (run 1 in Table I). In Table I are summarized the results of the generation of several heteroatom-substituted methyllithiums that were trapped with various electrophiles.[10] It should be noted that this lithium-tellurium exchange reaction proceeded satisfactorily in a variety of solvents, such as Et_2O, toluene, and hexane (runs 2-4). This is in marked contrast to the lithium-tin exchange reaction, which is sluggish in solvents of low polarity.[11] In the formation of

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[1] For reviews of α-heteroatom-substituted organometallics, see: (a) Pereyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworths: London, 1987; Chapter 9. (b) Kauffmann, T. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 410. (c) Krief, A. *Tetrahedron* **1980**, *36*, 2531. (d) Peterson, D. J. *Organomet. Chem. Rev.* **1972**, *A7*, 295.

[2] (a) Hiiro, T.; Kambe, N.; Ogawa, A.; Miyoshi, N.; Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1187. (b) Hiiro, T.; Mogami, T.; Kambe, N.; Fujiwara, S.-I.; Sonoda, N. *Synth. Commun.*, in press. (c) Hiiro, T.; Morita, Y.; Inoue, T.; Kambe, N.; Ogawa, A.; Ryu, I.; Sonoda, N. *J. Am. Chem. Soc.* **1990**, *112*, 455.

[3] (a) Shiner, C. S.; Tsunoda, T.; Goodman, B. A.; Ingham, S.; Lee, S.; Vorndam, P. E. *J. Am. Chem. Soc.* **1989**, *111*, 1381. (b) Sawyer, J. S.; Kucerovy, A.; Macdonald, T. L.; McGarvey, G. J. *J. Am. Chem. Soc.* **1988**, *110*, 842. (c) Quintard, J.-P.; Elissondo, B.; Hattich, T.; Pereyre, M. *J. Organomet. Chem.* **1985**, *285*, 149. (d) Corey, E. J.; Eckrich, T. M. *Tetrahedron Lett.* **1983**, *24*, 3163, 3165. (e) Cohen, T.; Matz, J. R. *J. Am. Chem. Soc.* **1980**, *102*, 6900. (f) Meyer, N.; Seebach, D. *Chem. Ber.* **1980**, *113*, 1290. (g) Still, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 1481.

[4] (a) Elissondo, B.; Verlhac, J.-B.; Quintard, J.-P.; Pereyre, M. *J. Organomet. Chem.* **1988**, *339*, 267. (b) Ahlbrecht, H.; Dollinger, H. *Tetrahedron Lett.* **1984**, *25*, 1353. (c) Peterson, D. J.; Ward, J. F. *J. Organomet. Chem.* **1974**, *66*, 209. (d) Peterson, D. J. *J. Am. Chem. Soc.* **1971**, *93*, 4027. (e) Peterson, D. J. *J. Organomet. Chem.* **1970**, *21*, P63.

[5] (a) Tessier-Youngs, C.; Beachley, O. T., Jr. *Inorg. Synth.* **1986**, *24*, 95. (b) Seitz, D. E.; Zapata, A. *Synthesis* **1981**, 557. (c) Dumont, W.; Krief, A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 161. (d) Chan, T. H.; Chang, E. *J. Org. Chem.* **1974**, *39*, 3264. (e) Brook, A. G.; Duff, J. M.; Anderson, D. G. *Can. J. Chem.* **1970**, *48*, 561. (f) Peterson, D. J. *J. Organomet. Chem.* **1967**, *9*, 373.

[6] (a) Kauffmann, T.; Echsler, K.-J.; Hamsen, A.; Kriegesmann, R.; Steinseifer, F.; Vahrenhorst, A. *Tetrahedron Lett.* **1978**, 4391. (b) Dolgoplosk, B. A.; Oreshkin, I. A.; Makovetsky, K. L.; Tinyakova, E. I.; Ostrovskaya, I. Ya.; Kershenbaum, I. L.; Chernenko, G. M. *J. Organomet. Chem.* **1977**, *128*, 339. Also see ref 5e.

[7] (a) Sato, T.; Matsuoka, H.; Igarashi, T.; Minomura, M.; Murayama, E. *J. Org. Chem.* **1988**, *53*, 1207. (b) Murayama, E.; Kikuchi, T.; Sasaki, K.; Sootome, N.; Sato, T. *Chem. Lett.* **1987**, 1897. (c) Kauffmann, T.; Kriegesmann, R.; Altepeter, B.; Steinseifer, F. *Chem. Ber.* **1982**, *115*, 1810. (d) Kauffmann, T.; Kriegesmann, R.; Woltermann, A. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 862.

[8] Seebach, D.; Beck, A. K. *Chem. Ber.* **1975**, *108*, 314.

[9] Tellurides were prepared as follows: **1a**-**e** from lithium butanetellurolate and (2-methoxyethoxy)methyl chloride, benzyl chloromethyl ether, dimethylmethyleneammonium chloride, (trimethylsilyl)methyl iodide, and dichloromethane, respectively, in THF; **1f**, according to the procedure depicted in eq 2 (run 15 in Table I).

[10] A typical reaction is as follows (run 1 in Table I): Into a solution of **1a** (1.0 mmol, 274 mg) in THF (5 mL) was added a 1.6 M hexane solution of butyllithium (1.0 mmol, 0.63 mL) at -78 °C. After 15 min, benzaldehyde (1.1 mmol, 117 mg) was added in one portion. The reaction mixture was warmed to 25 °C over a period of 1 h and then poured into a saturated aqueous NH_4Cl (30 mL) solution. The product was extracted with Et_2O (30 mL × 3) and dried over $MgSO_4$. Analysis of the mixture by GLC showed the formation of **3** in 86% yield. Subsequent radial layer chromatography on silica gel provided 137 mg (0.70 mmol, 70%) of **3** together with 183 mg (0.76 mmol, 76%) of dibutyl telluride. Runs 2-14 in Table I were carried out under identical conditions unless otherwise stated. The Li-Te exchange reaction proceeds very quickly and is complete within 15 min at -78 °C in THF and in ether. Only small amounts of the starting telluride (**1a**) remained unreacted in toluene (5%, run 3) and in hexane (12%, run 4). The yield of adduct **3** was not improved even when the exchange reaction was conducted for 1 h in hexane (see run 4).

[11] Seyferth, D.; Weiner, M. A. *J. Am. Chem. Soc.* **1962**, *84*, 361.

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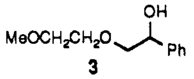
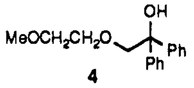
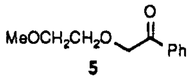
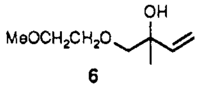
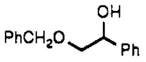
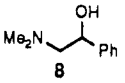
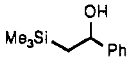
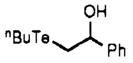
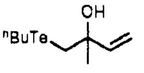
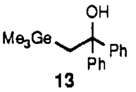
Table I. Preparation and Trapping of Heteroatom-Substituted Methyllithiums

run no.	eq. no.	starting material	GX	solvent	electrophile	product	yield, %[a]
1	1	MeOCH$_2$CH$_2$OCH$_2$Te^{n}Bu (**1a**)		THF	PhCHO	 **3**	70, 86[b]
2				Et$_2$O		**3**	69[b]
3				toluene		**3**	68[b]
4				hexane		**3**	37[b]
5				THF	Ph$_2$CO	 **4**	60
6					PhCOCl	 **5**	40
7					CH$_3$COCH=CH$_2$	 **6**	51
8		PhCH$_2$OCH$_2$Te^{n}Bu (**1b**)			PhCHO	 **7**	66
9		Me$_2$NCH$_2$Te^{n}Bu (**1c**)				 **8**	73
10		Me$_3$SiCH$_2$Te^{n}Bu (**1d**)				 **9**	89
11		^{n}BuTeCH$_2$Te^{n}Bu (**1e**)				 **10**	41, 73,[c] 81[c,d]
12					CH$_3$COCH=CH$_2$	 **11**	65[c,d]
13					Me$_3$SiCl	^{n}BuTeCH$_2$SiMe$_3$ (**1d**)	98[c–e]
14		^{n}Bu$_3$SnCH$_2$Te^{n}Bu (**1f**)		Et$_2$O		^{n}Bu$_3$SnCH$_2$SiMe$_3$ (**12**)	85[e,f]
15	2	CH$_2$Cl$_2$		THF	^{n}Bu$_3$SnCl	^{n}BuTeCH$_2$Sn^{n}Bu$_3$ (**1f**)	73[d]
16	3	**1e**	Me$_3$SiCl		PhCHO	**9**	63[c,d]
17		CH$_2$Cl$_2$				**9**	70[d]
18			Me$_3$GeBr		Ph$_2$CO	 **13**	83[d,e]

[a] Isolated yield. [b] GLC yield. [c] LiCl (1 equiv) was added. [d] Exchange reaction was performed at −95 °C. [e] NMR yield. [f] Reaction time 1 h.

^{n}BuTeCH$_2$Li (**2e**) from ^{n}BuTeCH$_2$Te^{n}Bu (**1e**), the yield of desired adduct **10** was dramatically improved when the reaction was conducted in the presence of LiCl[12] at −95 °C (run 11).[13] When methyl vinyl ketone was used as an electrophile, only 1,2-addition products were obtained, as shown in runs 7 and 12. What should be emphasized here is that ^{n}BuTeCH$_2$Sn^{n}Bu$_3$ (**1f**) underwent lithium–tellurium exchange rather than lithium–tin exchange, giving ^{n}Bu$_3$SnCH$_2$Li (**2f**), which was successfully trapped with chlorosilane in Et$_2$O to afford **12** in 85% yield (run 14).[14]

Since the reaction of lithium butanetellurolate[15] with dichloromethane yields **1e**[8,16] quantitatively with the concomitant formation of LiCl, use of the in situ formed **1e** offers a convenient method for the generation of **2e**. For example, **1f** was obtained in 73% yield (2.51 g, 5.14 mmol) after distillation, based on dichloromethane (7 mmol) used, without isolation of **1e** (see eq 2).

$$\mathrm{CH_2Cl_2} \xrightarrow{\mathrm{i}} \underset{\mathbf{1e}}{{}^n\mathrm{BuTeCH_2Te^nBu}} \xrightarrow[\mathrm{iii}]{\mathrm{ii}} \underset{\mathbf{1f},\ 73\%}{{}^n\mathrm{BuTeCH_2Sn^nBu_3}} \qquad (2)$$

reaction conditions: (i) CH$_2$Cl$_2$ (7 mmol), ^{n}BuTeLi (14 mmol), THF (30 mL), 0–67 °C, 2 h;
(ii) ^{n}BuLi (7 mmol), −95 °C, 10 min;
(iii) ^{n}Bu$_3$SnCl (7 mmol), −95 to +25 °C, 1.5 h

Attention should also be focused on the versatile potential of **1e** as a synthetic equivalent of methylene dianion, “$^-$CH$_2$$^-$”, that has two butyltelluro groups susceptible to an exchange reaction. As depicted by eq 3, two kinds of electrophiles could be successfully introduced via a repeated metalation/trapping sequence by a one-pot operation starting from **1e** (run 16) or from dichloromethane

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[12] Prepared in situ by the reaction of Me$_3$SiCl with butyllithium at 25 °C prior to the reaction.

[13] Villieras et al. observed that LiBr shows a similar effect in the generation of ClCH$_2$Li from ClCH$_2$Br and have suggested that added LiBr coordinates to the chlorine atom of formed ClCH$_2$Li and suppresses α-elimination of LiCl from ClCH$_2$Li: Tarhouni, R.; Kirschleger, B.; Rambaud, M.; Villieras, J. *Tetrahedron Lett.* **1984**, *25*, 835.

[14] Bis(tributylstannyl)methane was also formed in ca. 12% yield, probably via Li–Sn exchange between **12** and **2f**, giving the (silylmethyl)lithium **2d**, together with a trace amount of ^{n}Bu$_4$Sn (<2%). When a similar reaction was conducted in THF, bis(tributylstannyl)methane was obtained as the major product (ca. 50%).

[15] (a) Engman, L.; Cava, M. P. *Synth. Commun.* **1982**, *12*, 163. (b) Piette, J. L.; Renson, M. *Bull. Soc. Chim. Belg.* **1970**, *79*, 353, 367, 383; *Chem. Abstr.* **1970**, *73*, 66199, 66200, 66201. (c) Petragnani, N.; de Moura Campos, M. *Chem. Ber.* **1963**, *96*, 249.

[16] Hope, E. G.; Kemmitt, T.; Levason, W. *Organometallics* **1988**, *7*, 78.

$$\mathrm{CH_2Cl_2} \xrightarrow{\text{i-iii}} \underset{\mathbf{1}}{\mathrm{G{-}CH_2{-}Te^nBu}} \xrightarrow{\text{iv, v}} \mathrm{G{-}CH_2{-}E} \qquad (3)$$

reaction conditions: (i) ^{n}BuTeLi, 6c, 2 h;
(ii) ^{n}BuLi, -95 °C, 10 min;
(iii) GX, -95 to +25 °C, 1 h;
(iv) ^{n}BuLi, -95 to -78 °C, 20 min;
(v) electrophile (E^+), -78 to +25 °C, 1 h

(runs 17 and 18). Bis(phenyltelluro)methane, a precursor of $PhTeCH_2Li$,[8] was not suitable for this purpose.[17]

The present method is operationally simple and has wide generality, and so it will be a practical and quite useful procedure for the preparation of various heteroatom-substituted methyllithiums.

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[17] The reaction of $PhTeCH_2SiMe_3$ with butyllithium gave PhLi predominantly rather than **2d** in about a 2:1 ratio (determined by trapping with PhCHO), probably because the thermodynamic stability of PhLi may be comparable to that of **2d**.

Synthesis, Structure, and Reactivity of the First Anionic Acyldihalocarbonyliron(II) Complex. Halogen-Induced Insertion of Carbon Monoxide into an Alkyl-Iron Bond

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Summary: The reaction of $[PPN][RFe(CO)_4]$ (R = CH_3 (**1a**), C_2H_5 (**1b**), $PhCH_2$ (**1c**)) with iodine in CH_2Cl_2 induces the insertion of carbon monoxide into the carbon-metal bond to give the first $[PPN][RCOFe(CO)_3I_2]$ complexes (**3a-c**). The molecular structure of **3a** was established by X-ray analysis. $[PPN][RCOFe(CO)_4]$ (**4a-d**) reacts with I_2 in CH_2Cl_2 to give $[PPN][RCOFe(CO)_3I_2]$ (**3a-d**) in high yield. $[PPN]_2[Fe_4(CO)_{13}]$ (**2**) reacts with methyl iodide to give **3a**. Reactions of **3** with nucleophiles such as alcohols and amines have been investigated.

Insertion of carbon monoxide into a metal-alkyl bond, giving an acyl-metal complex, is a fundamental reaction in organometallic chemistry.[1] It is known that an anionic alkyliron complex, $[RFe(CO)_4]^-$ (**1**), reacts with alcohols, amines, and water in the presence of an excess of iodine or bromine to give esters, amides, and carboxylic acids, respectively (eq 1).[2] In the course of our studies on iron

$$\underset{\mathbf{1}}{[RFe(CO)_4]^-} + NuH + X_2 \rightarrow RCONu \qquad (1)$$

$$NuH = R'OH,\ R'NH_2,\ H_2O;\ X_2 = Br_2,\ I_2$$

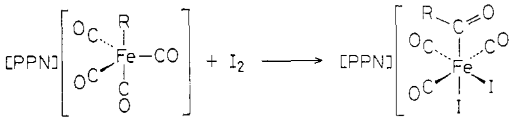
cluster carbonylates,[3] we now have found that the reaction of $[PPN]_2[Fe_4(CO)_{13}]$ (**2**) with methyl iodide gives $[PPN][CH_3COFe(CO)_3I_2]$ (**3a**). This complex may be an intermediate in the reaction shown in eq 1. For this reason we also examined the reactions of $[RFe(CO)_4]^-$ (**1**) with iodine and found that the same complex is formed and, thus, clear evidence for I_2-induced CO insertion into an alkyl-metal bond was obtained. We now report the preparation, structure, and reactivities of the novel complex **3**.

$[PPN]_2[Fe_4(CO)_{13}]$ (**2**) reacted with an excess of methyl iodide in THF under an argon atmosphere at 25 °C during the course of 5 days to give $[PPN][CH_3COFe(CO)_3I_2]$ (**3a**)

$$\underset{\mathbf{2}}{[PPN]_2[Fe_4(CO)_{13}]} + CH_3I \rightarrow \underset{\mathbf{3a}}{[PPN][CH_3COFe(CO)_3I_2]} \qquad (2)$$

in 60% yield. Thus, the tetranuclear cluster decomposed completely to the mononuclear complex to give the first acyldiiodotricarbonylferrate(II) complex **3**.

Such complex salts also could be prepared by reaction of salts of $[RFe(CO)_4]^-$ anions with iodine. For example, $[PPN][CH_3Fe(CO)_4]$ (**1a**), $[PPN][C_2H_5Fe(CO)_4]$ (**1b**), and $[PPN][PhCH_2Fe(CO)_4]$ (**1c**) reacted with I_2 in CH_2Cl_2 at -78 °C during the course of 2-4 h to give $[PPN][CH_3COFe(CO)_3I_2]$ (**3a**; yield 33%), $[C_2H_5COFe(CO)_3I_2]$ (**3b**; yield 45%), and $[PPN][PhCH_2COFe(CO)_3I_2]$ (**3c**; yield 40%), respectively (eq 3). $[PPN][RCOFe(CO)_4]$ (**4**; R = CH_3 (**4a**), C_2H_5 (**4b**), $PhCH_2$ (**4c**), Ph (**4d**)) also reacted with I_2 in CH_2Cl_2 at -78 °C to give the same products, $[PPN][RCOFe(CO)_3I_2]$ (yield 95% (**3a**), 75% (**3b**), 69% (**3c**), 87% (**3d**)), with evolution of carbon monoxide (eq 4).



1 3 (3)

$$\underset{\mathbf{4}}{[PPN][RCOFe(CO)_4]} + I_2 \rightarrow \underset{\mathbf{3}}{[PPN][RCOFe(CO)_3I_2]} + CO \qquad (4)$$

Reactions of the complex salts **1** or **4** with bromine in a similar fashion gave the corresponding anionic acyldibromotricarbonyliron complexes at -78 °C, which was confirmed by IR spectra of the reaction solutions.[4]

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[1] E.g.: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 355.

[2] (a) Takegami, Y.; Watanabe, Y.; Masada, I.; Kanaya, I. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1456. (b) Masada, H.; Mizuno, M.; Suga, S.; Watanabe, Y.; Takegami, Y. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3824. (c) Collman, J. P.; Winter, S. R.; Komoto, R. G. *J. Am. Chem. Soc.* **1973**, *95*, 249. (d) Collman, J. P. *Acc. Chem. Res.* **1975**, *8*, 342.

[3] Ishihara, A.; Mitsudo, T.; Watanabe, Y. *J. Organomet. Chem.* **1989**, *368*, 199 and references cited therein.

[4] For $[PPN][PhCOFe(CO)_3Br_2]$ in CH_2Cl_2, derived from $[PPN][PhCOFe(CO)_4]$ (**4d**) and Br_2 (at 0 °C), $\nu(C{\equiv}O)$ = 2097 (s), 2037 (vs), 1995 (s) cm^{-1} and $\nu(C{=}O)$ = 1603 (m) cm^{-1}. This complex decomposed in CH_2Cl_2 solution at 10 °C to give benzoyl bromide ($\nu(C{=}O)$ = 1773 cm^{-1}). For $[PPN][CH_3COFe(CO)_3Br_2]$ in CH_2Cl_2, derived from $[PPN][CH_3Fe(CO)_4]$ (**1a**) and Br_2 (at 0 °C), $\nu(C{\equiv}O)$ = 2097 (s), 2031 (vs), 1995 (s) cm^{-1} and $\nu(C{=}O)$ = 1647 (m), 1628 (m) cm^{-1}. This complex decomposed in CH_2Cl_2 solution at 10 °C to give acetyl bromide ($\nu(C{=}O)$ = 1811 cm^{-1}).