

sugars as building blocks for replicating systems, these results direct thinking once again toward ribose itself, and chemical work seeking an improved abiotic synthesis of ribose would be most desirable.

(16) **Note Added in Proof:** In the synthesis of these oligomers, coupling yields were ca. 90% for glycerothymine and >99% for natural nucleosides. The product oligonucleotides were purified by reversed phase HPLC (Nucleosil C-4 column, gradient from 15% to 30% acetonitrile in 0.1 M triethylammonium acetate) prior to the removal of the 5'-trityl groups and detritylated (80% acetic acid). Samples of the oligonucleotides containing the flexible base were digested with spleen phosphodiesterase, snake venom phosphodiesterase, and bacterial alkaline phosphatase. HPLC of the digests showed the expected nucleosides in their expected ratios.

## A New Access to Acyl- and Aroyllithiums via Lithium-Tellurium Exchange

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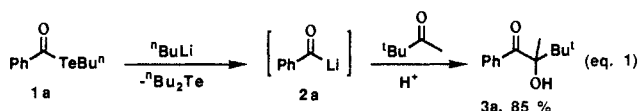
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The most straightforward method for nucleophilic introduction of acyl and aroyl groups into organic molecules is the use of carbonyl anions, represented by acyl- and aroyllithiums, as nucleophiles.<sup>1</sup> Their synthetic utility, however, has been severely limited for a long time because of difficulty both in their generation and in control of their reaction courses.<sup>2,3</sup> Notable advances in this chemistry appeared in the 1980s.<sup>3,4</sup> In 1982, Seyferth et al. succeeded in an efficient intermolecular trapping of acyllithiums under carefully controlled reaction conditions.<sup>3a-f</sup> Shortly after, Murai and we disclosed a unique intramolecular conversion of acyllithiums into lithium enolates based on 1,2-silicon shift.<sup>3g</sup> As for the methodology for generation of acyl- and aroyllithiums, there are only two methods available so far.<sup>5</sup> One is the reaction of organolithiums with carbon monoxide,<sup>2,3</sup> and the other is the direct lithiation of carbonyl carbon by abstraction of a formyl hydrogen.<sup>4</sup> In this paper we report a novel and practically useful entry to acyl- and aroyllithiums **2** based on efficient lithium-

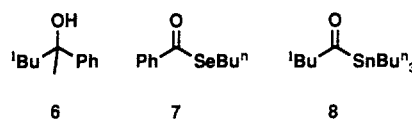
tellurium exchange<sup>6,7</sup> of telluroesters **1**, which are easily accessible from the corresponding acid chlorides and telluroate anions.<sup>8</sup>

When butyllithium was added to *Te*-butyl tellurobenzoate (**1a**) in THF/Et<sub>2</sub>O (10/8) at -105 °C in the presence of pinacolone as an electrophile,  $\alpha$ -hydroxy ketone **3a** was obtained in 85% yield together with dibutyl telluride (82%) (entry 1 in Table I).<sup>9</sup> This simple benzoyllithium cannot be trapped efficiently by the PhLi/CO method.<sup>3d</sup>



Under similar conditions, [*p*-(trifluoromethyl)benzoyl]lithium and (2,6-difluorobenzoyl)lithium (**2b,c**) can be generated from the corresponding tellurides (**1b,c**) in good yields (entries 3 and 4). Efficient generation of acyllithiums bearing no  $\alpha$ -hydrogen, e.g., pivaloyllithium and (1-adamantylcarbonyl)lithium (**2d,e**), has been attained also (entries 5-11). In the case of acyllithiums, reactions at -78 °C using *tert*-butyllithium gave favorable results when pinacolone was used as an electrophile (entries 5-7 and 11). Chlorotrimethylsilane is also a suitable electrophile, and the desired product, acylsilane **4**, was formed in good yield by using butyllithium at -105 °C (entry 8). Use of pivalaldehyde as an electrophile afforded a poor yield of  $\alpha$ -hydroxy ketone **5** due to rapid addition of *tert*-butyllithium to the aldehyde (entry 10). Although *Te*-butyl octanetelluroate gave octanoyltrimethylsilane in only ca. 10% yield under conditions similar to those of entry 8, the exchange reaction might have proceeded efficiently because an almost quantitative amount of dibutyl telluride was obtained from the resulting mixture.

In order to test the stability and the reactivity of benzoyllithium, we subsequently added pinacolone to the mixture obtained by the reaction of **1a** with butyllithium performed at -105 °C in THF/Et<sub>2</sub>O for 1 min. The result that **3a** (16%), benzoin [34%, via dimerization of in situ formed benzoyllithium (**2a**)],<sup>2</sup> and benzil (21%, probably derived by the reaction of **2a** with **1a**) were formed, together with 81% of dibutyl telluride, indicates that benzoyllithium is extremely reactive, having a lifetime much shorter than 1 min, even at -105 °C. The fact that benzene and alcohol **6** were not detected from the resulting mixture suggests that elimination of carbon monoxide from **2a** leading to phenyllithium may be ruled out under these conditions.<sup>10</sup>



(1) For a recent review for synthetic equivalents of acyl and aroyl anions, see: Ager, D. J. In *Unpoled Synthons*; Hase, T. A., Ed.; Wiley-Interscience: New York, 1987; Chapter 2 and references cited therein.

(2) (a) Wittig, G. *Angew. Chem.* **1940**, *53*, 241, footnote 58. (b) Ryang, M.; Tsutsumi, S. *Bull. Chem. Soc. Jpn.* **1962**, *35*, 1121. (c) Jutzki, P.; Schröder, F.-W. *J. Organomet. Chem.* **1970**, *24*, 1. (d) Trzupke, L. S.; Newirth, T. L.; Kelly, E. G.; Sbarbati, N. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1973**, *95*, 8118. (e) Nudelman, N. S.; Vitale, A. A. *J. Organomet. Chem.* **1983**, *241*, 143. For a review, see: (f) Narayana, C.; Periasamy, M. *Synthesis* **1985**, 253.

(3) (a) Seyferth, D.; Weinstein, R. M. *J. Am. Chem. Soc.* **1982**, *104*, 5534. (b) Seyferth, D.; Weinstein, R. M.; Wang, W.-L. *J. Org. Chem.* **1983**, *48*, 1144. (c) Weinstein, R. M.; Wang, W.-L.; Seyferth, D. *Ibid.* **1983**, *48*, 3367. (d) Seyferth, D.; Wang, W.-L.; Hui, R. C. *Tetrahedron Lett.* **1984**, *25*, 1651. (e) Seyferth, D.; Hui, R. C. *J. Org. Chem.* **1985**, *50*, 1985. (f) Seyferth, D.; Hui, R. C. *J. Am. Chem. Soc.* **1985**, *107*, 4551. (g) Murai, S.; Ryu, I.; Iriguchi, J.; Sonoda, N. *Ibid.* **1984**, *106*, 2440.

(4) Shiner, C. S.; Berks, A. H.; Fisher, A. M. *J. Am. Chem. Soc.* **1988**, *110*, 957.

(5) Heathcock et al. suggested that aroyl anions might be formed by the reaction of acylsilanes with fluoride ion, where corresponding adducts were obtained in the presence of electrophiles. Alternative mechanisms have been also postulated. (a) Schinzer, D.; Heathcock, C. H. *Tetrahedron Lett.* **1981**, *22*, 1881. (b) Degl'Innocenti, A.; Pike, S.; Walton, D. R. M.; Seconi, G.; Ricci, A.; Fiorenza, M. *J. Chem. Soc., Chem. Commun.* **1980**, 1201. (c) DePuy, C. H.; Bierbaum, V. M.; Damrauer, R.; Soderquist, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 3385. (d) Page, P. C. B.; Rosenthal, S.; Williams, R. V. *Tetrahedron Lett.* **1987**, *28*, 4455.

(6) For our previous papers on lithium-tellurium exchange, see: (a) Hiroy, T.; Kambe, N.; Ogawa, A.; Miyoshi, N.; Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1187. (b) Hiroy, T.; Mogami, T.; Kambe, N.; Fujiwara, S.-I.; Sonoda, N. *Synth. Commun.*, in press.

(7) Reich et al. suggested that the lithium-tellurium exchange reaction proceeds via ate complexes: (a) Reich, H. J.; Green, D. P.; Phillips, N. H. *Proceedings of Pre-Ichac Ube Conference Held at Ube*; July 16-18, 1987; pp 24-34. For recent reports on the intermediacy of ate complexes in lithium-metal and lithium-metalloid exchange, see: (b) Reich, H. J.; Phillips, N. H.; Reich, I. L. *J. Am. Chem. Soc.* **1985**, *107*, 4101. (c) Reich, H. J.; Phillips, N. H. *Ibid.* **1986**, *108*, 2102. (d) Reich, H. J.; Phillips, N. H. *Pure Appl. Chem.* **1987**, *59*, 1021. (e) Reich, H. J.; Green, D. P.; Phillips, N. H. *J. Am. Chem. Soc.* **1989**, *111*, 3444.

(8) Telluroesters **1** were prepared by the reaction of lithium (**1a,d,e**) or sodium (**1b,c**) butanetelluroates with the corresponding acid chlorides according to the following literature: (a) Piette, J. L.; Renson, M. *Bull. Soc. Chim. Belg.* **1970**, *79*, 383; *Chem. Abstr.* **1970**, *73*, 66201. (b) Piette, J. L.; Debergh, D.; Baiwir, M.; Llabres, G. *Spectrochim. Acta* **1980**, *36A*, 769. (c) Gardner, S. A.; Gysling, H. J. *J. Organomet. Chem.* **1980**, *197*, 111.

(9) The result clearly indicates that butyllithium attacked Te atom exclusively affording benzoyllithium (**2a**), which then reacted with pinacolone to give **3a**. For other byproducts formed, see supplementary material.

**Table I.** Trapping of Acyllithiums and Aroyllithiums Generated by Lithium–Tellurium Exchange

$1 \xrightarrow[\text{temp, solv}]{\text{BuLi}} \left[ \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{Li} \right] \xrightarrow[30 \text{ min}]{\text{electrophile}} \text{product}$							
entry	substrate	electrophile (1.5 equiv)	product	BuLi (equiv)	temp, °C	solv	yield, <sup>a</sup> %
1				<sup>n</sup> BuLi (1.2)	-105	THF/Et <sub>2</sub> O	85
2				<sup>n</sup> BuLi (1.2)	-78	THF	45 <sup>b</sup>
3					-105	THF/Et <sub>2</sub> O	60
4				<sup>n</sup> BuLi (1.2)	-105	THF/Et <sub>2</sub> O	74
5				<sup>n</sup> BuLi (1.2)	-105	THF/Et <sub>2</sub> O	trace <sup>c</sup>
6				<sup>t</sup> BuLi (1.6)	-105	THF/Et <sub>2</sub> O	27
7					-78	THF	66
8		Me <sub>3</sub> SiCl		<sup>n</sup> BuLi (1.2)	-105	THF/Et <sub>2</sub> O	65 <sup>b</sup> (70) <sup>b,d</sup>
9					-78	THF	10 <sup>b</sup>
10		<sup>t</sup> BuCHO		<sup>t</sup> BuLi (1.6)	-78	THF	25 <sup>e</sup>
11				<sup>t</sup> BuLi (1.6)	-78	THF	57

<sup>a</sup> Isolated yield based on telluroesters. <sup>b</sup> GLC yield. <sup>c</sup> Addition of <sup>n</sup>BuLi to pinacolone predominated. <sup>d</sup> HMPA (3 equiv) was added. <sup>e</sup> 2,2,4,4-Tetramethyl-3-pentanol was obtained in ca. 40% yield based on pivalaldehyde used.

Although corresponding selenoesters and acylstannanes can also be the candidates for precursors of carbonyl anions, reactions of **7** and **8** under similar conditions did not give desired adducts **3a** and **3d**.<sup>11</sup>

In summary, a novel method for generation of acyl- and aroyllithiums has been established by the use of a lithium-tellurium exchange reaction.<sup>12</sup> This success may be based on the extremely

(10) Ab initio calculations showed that the following reaction was exothermic. The optimized structure of the acyllithium has one of the C–H bonds eclipsed with the carbonyl group. Li has an intramolecular interaction with oxygen ( $\angle \text{O}=\text{C}-\text{Li} = 61.3^\circ$ ), as demonstrated in the case of formyllithium: Kaufmann, E.; Schleyer, P. v. R.; Gronert, S.; Streitwieser, A., Jr.; Halpern, M. *J. Am. Chem. Soc.* **1987**, *109*, 2553.

CH <sub>2</sub> Li + CO	CH <sub>2</sub> CLi	ΔE (kcal/mol)
basis set		
3-21 G//3-21 G		-24.1
6-311+G**/3-21 G		-11.2
MP2/6-311+G**/3-21 G		-15.7

(11) Under the same conditions as in entry 1, **7** gave only a trace amount of dibutyl selenide (<1%). In this case, reaction of **7** with the lithium enolate of pinacolone predominated. In the case of **8**, considerable amounts of tetrabutylstannane (up to 30%) were obtained. This result may suggest that lithium–tin exchange might proceed to some extent.

high reactivity of organotellurium compounds toward alkyl-lithiums. Since telluroesters **1** are stable and easily accessible, the present method is practically quite useful for generation of a variety of acyl- and aroyllithiums which are thermodynamically somewhat stable but kinetically quite reactive.

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**Supplementary Material Available:** A typical experimental

(12) The actual acylating and aroylating species would probably be free acyl- and aroyllithiums rather than their tellurium ate complexes, which are likely to be the transient intermediates in lithium–tellurium exchange,<sup>7</sup> because product ratios of 1,2-addition over 1,4-addition to methyl vinyl ketone in the present system using *Te*-butyl 2,2-dimethylpropanetelluroate (2.2 at -110 °C in THF/Et<sub>2</sub>O and 5.0 at -78 °C in THF) were quite similar to those in a <sup>t</sup>BuLi/CO system (1.9 and 5.5, respectively). For details and discussion, see the supplementary material.

(13) Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. Carnegie-Mellon Chemistry Publishing Unit, Pittsburgh, PA, 1984.

procedure, full characterization of telluroesters,  $\alpha$ -hydroxy ketones, and an acylsilane obtained, and a discussion on actual acylating species and main side reactions (8 pages). Ordering information is given on any current masthead page.

### Effects of Metal and Ligand Substitutions on Gas-Phase Acidities of Transition-Metal Hydrides

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Gas-phase chemistry and spectroscopy of negative ions have provided important data on thermochemistry and reactivity for a wide variety of transition-metal organometallic complexes.<sup>1-6</sup> Despite this, since the work of Stevens Miller and Beauchamp,<sup>7</sup> who determined the gas-phase acidities of HMn(CO)<sub>5</sub>, H<sub>2</sub>Fe(CO)<sub>4</sub>, and HCo(CO)<sub>4</sub>, no further acidities for transition-metal hydride complexes have been reported. This is particularly surprising since hydrides are very important in reactive and catalytic chemistry.<sup>8</sup> We report here the determination of the gas-phase acidity of HRe(CO)<sub>5</sub>, a refinement in the value for the gas-phase acidity of HMn(CO)<sub>5</sub>, and experiments identifying HMn(CO)<sub>3</sub>(PF<sub>3</sub>)<sub>2</sub>, HMn(CO)<sub>2</sub>(PF<sub>3</sub>)<sub>3</sub>, HCo(PF<sub>3</sub>)<sub>4</sub>, and HIr(PF<sub>3</sub>)<sub>4</sub> as extremely strong gas-phase acids.

The hydrides were synthesized as described in the literature.<sup>11-16</sup> HIr(PF<sub>3</sub>)<sub>4</sub> showed an unidentified low-mass contaminant in some of the samples we prepared, but all other compounds gave pure samples. The ion-molecule reactions were studied at the Geophysics Laboratory, using a selected-ion flow tube described elsewhere.<sup>17</sup> Proton abstraction reactions by the metal anions were not studied since the metal compounds decompose in the ion source.

The hydride HMn(CO)<sub>5</sub> proton transfers to F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, and CCl<sub>3</sub>CO<sub>2</sub><sup>-</sup>, at rates near the collision frequency.<sup>18</sup> No reaction is observed with I<sup>-</sup>. HRe(CO)<sub>5</sub> reacts rapidly by proton transfer

**Table I.** Gas-Phase Acidity Scale Used for This Work, with the Relative Positions of the Transition-Metal Hydrides Given<sup>a</sup>

acid	$\Delta H_{\text{acid}}$	$\Delta G_{\text{acid}}$
HF	371.5 ± 0.2	365.7 ± 0.5
HCO <sub>2</sub> H	345.2 ± 2.3	338.2 ± 2.0
HNO <sub>2</sub>	338.2 ± 4.3	330.5 ± 4.6
HCl	333.4 ± 0.2	328.0 ± 0.5
HRe(CO) <sub>5</sub>	position according to this work	
CHF <sub>2</sub> CO <sub>2</sub> H	330.0 ± 2.3	323.5 ± 2.0
CF <sub>3</sub> COCH <sub>2</sub> COCH <sub>3</sub>	328.4 ± 4.1	322.0 ± 2.0
CHCl <sub>2</sub> CO <sub>2</sub> H	327.3 ± 2.6	320.8 ± 2.0
HBr	323.5 ± 0.1	318.2 ± 0.4
CCl <sub>3</sub> CO <sub>2</sub> H	319.9 ± 2.9	312.8 ± 2.0
HMn(CO) <sub>5</sub>	position according to this work	
HI	314.4 ± 0.1	309.3 ± 0.4
HPO <sub>3</sub>	311 ± 3 <sup>b</sup>	
HMn(CO) <sub>3</sub> (PF <sub>3</sub> ) <sub>2</sub> , HMn(CO) <sub>2</sub> (PF <sub>3</sub> ) <sub>3</sub>	positions according to this work	
FSO <sub>3</sub> H	b	
HIr(PF <sub>3</sub> ) <sub>4</sub>	position according to this work	
CF <sub>3</sub> SO <sub>3</sub> H	b	
HCo(PF <sub>3</sub> ) <sub>4</sub>	position according to this work	

<sup>a</sup>The acidity data, in kilocalories per mole, are from refs 9 and 10 except as noted. <sup>b</sup>Reference 19.

to F<sup>-</sup>, HCO<sub>2</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, and Cl<sup>-</sup>. In the reaction with F<sup>-</sup>, ligand displacement also occurs, with ion products (CO)<sub>5</sub>Re<sup>-</sup> (65%) and HRe(CO)<sub>3</sub>F<sup>-</sup> (35%). HRe(CO)<sub>5</sub> reacts by proton transfer with CHF<sub>2</sub>CO<sub>2</sub><sup>-</sup>, but at a rate about a factor of 3 less than collisional. No reaction is observed with CF<sub>3</sub>COCHCOCH<sub>3</sub><sup>-</sup>, CHCl<sub>2</sub>CO<sub>2</sub><sup>-</sup>, Br<sup>-</sup>, or I<sup>-</sup>.

A mixture of HMn(CO)<sub>3</sub>(PF<sub>3</sub>)<sub>2</sub> and HMn(CO)<sub>2</sub>(PF<sub>3</sub>)<sub>3</sub> reacts rapidly with Br<sup>-</sup>, I<sup>-</sup>, and PO<sub>3</sub><sup>-</sup>, and a factor of 30 more slowly with FSO<sub>3</sub><sup>-</sup>. Proton transfer occurs to all the ions, but the mixture also shows product masses 455 ± 10 amu and 475 ± 10 amu from reaction with PO<sub>3</sub><sup>-</sup>, and ion products of mass 325 ± 10 amu and 403 ± 10 amu from reaction with FSO<sub>3</sub><sup>-</sup>. No reaction occurs with CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>.

HCo(PF<sub>3</sub>)<sub>4</sub> proton transfers at collision frequency to I<sup>-</sup>, PO<sub>3</sub><sup>-</sup>, FSO<sub>3</sub><sup>-</sup>, and CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>. HIr(PF<sub>3</sub>)<sub>4</sub> proton transfers rapidly to Br<sup>-</sup>, I<sup>-</sup>, PO<sub>3</sub><sup>-</sup>, and FSO<sub>3</sub><sup>-</sup>, and a factor of 1000 more slowly to CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>.

Table I gives the gas-phase acidity scale<sup>9,10,19</sup> used for this work. The positions of the hydride acidities are determined by assuming that the reaction is exothermic if the proton-transfer rate is equal to the ion-molecule collision rate,<sup>18</sup> and endothermic if the rate is much smaller than the collisional rate.<sup>20</sup>

The acidity of HMn(CO)<sub>5</sub> was previously bracketed between the acidities of HI and CF<sub>3</sub>CO<sub>2</sub>H.<sup>7</sup> The present work confirms that result, but narrows the bracketing slightly, to between HI and CCl<sub>3</sub>CO<sub>2</sub>H ( $\Delta H_{\text{acid}} = 314-320$  kcal/mol). The third-row complex HRe(CO)<sub>5</sub> has an acidity,  $\Delta H_{\text{acid}}$ , between 330 and 333 kcal/mol, or about 10-19 kcal/mol less acidic than HMn(CO)<sub>5</sub>. Meckstroth and Ridge<sup>21</sup> presented evidence that the electron affinities of (CO)<sub>5</sub>Mn and (CO)<sub>5</sub>Re are equal. The acidity difference between HMn(CO)<sub>5</sub> and HRe(CO)<sub>5</sub> therefore is a result of the homolytic bond energy  $D[(\text{CO})_5\text{Re}-\text{H}]$  being 10-19 kcal/mol stronger than  $D[(\text{CO})_5\text{Mn}-\text{H}]$ . Using  $D[(\text{CO})_5\text{Mn}-\text{H}] = 60$  kcal/mol<sup>22</sup> gives  $D[(\text{CO})_5\text{Re}-\text{H}] = 70-79$  kcal/mol. These energetics are in keeping with the less acidic

- (1) Gregor, I. K.; Guilhaus, M. *Mass Spectrom. Rev.* **1984**, *3*, 39.
- (2) Squires, R. R. *Chem. Rev.* **1987**, *87*, 623.
- (3) Sallans, L.; Lane, K. R.; Freiser, B. S. *J. Am. Chem. Soc.* **1989**, *111*, 865.
- (4) Dillow, G. W.; Nicol, G.; Kebarle, P. *J. Am. Chem. Soc.* **1989**, *111*, 5465.
- (5) Pan, Y. H.; Ridge, D. P. *J. Am. Chem. Soc.* **1989**, *111*, 1150. Jones, M. T.; McDonald, R. N.; Schell, P. L.; Ali, M. H. *J. Am. Chem. Soc.* **1989**, *111*, 5983.
- (6) Marotta, C. J.; Tsai, C.-p.; McFadden, D. L. *J. Chem. Phys.* **1989**, *91*, 2194.
- (7) Stevens Miller, A. E.; Beauchamp, J. L. *J. Am. Chem. Soc.*, submitted; cited in refs. 1, 2, 6, 8-10.
- (8) Pearson, R. G. *Chem. Rev.* **1985**, *85*, 41.
- (9) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *Gas Phase Ion and Neutral Thermochemistry. J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.
- (10) Bartmess, J. E., personal communication, 1987.
- (11) Warner, K. E.; Norton, J. R. *Organometallics* **1985**, *4*, 2150.
- (12) Miles, W. J.; Clark, R. J. *Inorg. Chem.* **1968**, *7*, 1801.
- (13) Udovich, C. A.; Clark, R. J. *Inorg. Chem.* **1969**, *8*, 938.
- (14) Sternberg, H. W.; Wender, I.; Friedel, R. A.; Orchin, M. *J. Am. Chem. Soc.* **1953**, *75*, 2717.
- (15) van der Ent, A.; Onderdelinden, A. L. *Inorg. Synth.* **1973**, *14*, 92.
- (16) Bennett, M. A.; Patmore, D. J. *Inorg. Chem.* **1971**, *10*, 2387.
- (17) Viggiano, A. A.; Paulson, J. F. *J. Chem. Phys.* **1983**, *79*, 2241.
- (18) Rates of proton transfer were determined for all reactions reported here and can be compared to a theoretical ion-molecule collision frequency by using the method of Su and Chesnavich: Su, T.; Chesnavich, W. J. *J. Chem. Phys.* **1982**, *76*, 583.

(19) Henchman, M.; Viggiano, A. A.; Paulson, J. F.; Freedman, A.; Wormhoudt, J. *J. Am. Chem. Soc.* **1985**, *107*, 1453. Adams, N. G.; Smith, D.; Viggiano, A. A.; Paulson, J. F.; Henchman, M. *J. Chem. Phys.* **1986**, *84*, 6728. Paulson, J. F.; Viggiano, A. A.; Henchman, M.; Dale, F. In *Symposium on Atomic and Surface Physics*; Obertraun, Austria, February 1986; Horwoka, F., Lindinger, W., Märk, T. D., Eds.; Studienförderungsgesellschaft M.b.H.: Josef Hirnstrasse 7, A6020 Innsbruck.

(20) Han, C.-C.; Brauman, J. I. *J. Am. Chem. Soc.* **1989**, *111*, 6491 and references therein.

(21) Meckstroth, W. K.; Ridge, D. P. *J. Am. Chem. Soc.* **1985**, *107*, 2281.

(22) Determined from the ionization potential of Mn(CO)<sub>5</sub> of 7.7 eV (Martinho Simões, J. A.; Schultz, J. C.; Beauchamp, J. L. *Organometallics* **1985**, *4*, 1238) and an appearance potential of (CO)<sub>5</sub>Mn<sup>+</sup> from (CO)<sub>5</sub>MnH of 10.3 eV (Stevens, A. E. Ph.D. Thesis, California Institute of Technology, 1981). A somewhat lower value is given by Connor et al.: Connor, J. A.; Zafarani-Moattar, M. T.; Bickerton, J.; El Saied, N. I.; Suradi, S.; Carson, R.; Al Takhin, G.; Skinner, H. A. *Organometallics* **1982**, *1*, 1166.