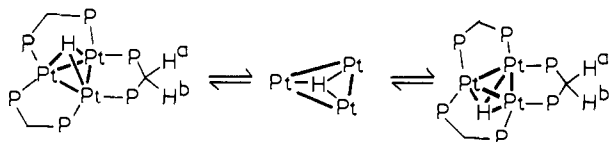


$^1\text{H}$  NMR are unchanged, this process probably involves a direct inversion of the  $\text{Pt}_3(\mu_3\text{-H})$  unit (eq 1).<sup>14</sup> The activation energy



for this process is calculated to be  $\Delta G^\ddagger = 50 \pm 1 \text{ kJ mol}^{-1}$  ( $T_c = -24^\circ\text{C}$  at 100 MHz) and can be compared with  $\Delta G^\ddagger = 46.5 \text{ kJ mol}^{-1}$  for inversion of the  $\text{Pt}_2(\mu\text{-H})$  unit in the  $[\text{Pt}_2\text{H}_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$  ion.<sup>15</sup>

The cation **3** as the  $[\text{PF}_6]^-$  salt could also be prepared by reduction of **1** with Na/Hg in tetrahydrofuran, followed by protonation with  $\text{NH}_4[\text{PF}_6]$ . It is possible that this reaction proceeds via the expected  $[\text{Pt}_3(\mu\text{-dppm})_3]$  in which the planar  $\text{Pt}_3\text{L}_6$  system is isolobal with cyclopropane.<sup>17</sup>

Complex **2** could be prepared by bubbling CO through a solution of **3** and could be converted back to **3** by flushing the solution of **2** with nitrogen for several hours. It was characterized by the  $^1\text{H}$ ,  $^{31}\text{P}$ , and  $^{195}\text{Pt}$  NMR spectra.<sup>11,14</sup> The presence of the  $\text{Pt}_3(\mu_3\text{-H})$  group was confirmed by the  $^1\text{H}$  NMR at  $20^\circ\text{C}$  [ $\delta -1.04$ , septet,  $^2J(\text{PH}) = 4.5$ ,  $^1J(\text{PtH}) = 598 \text{ Hz}$ ] and by the  $^1\text{H}$ -coupled  $^{195}\text{Pt}$  NMR spectra,<sup>14</sup> and the presence of CO was confirmed by the IR spectrum [ $\nu(\text{CO}) = 1982 \text{ cm}^{-1}$ , cf.  $\nu(\text{CO})$  for **1** =  $1750 \text{ cm}^{-1}$ ].<sup>8</sup> At  $-60^\circ\text{C}$  the  $^1J(\text{PtH})$  coupling was reduced to 573 Hz and the chemical shift was  $\delta -1.47$ . Further characterization was obtained by treating **3** with  $^{13}\text{CO}$  to give **2\*** ( $^* = ^{13}\text{CO}$  labeled). At  $-90^\circ\text{C}$ , the hydride signal was at  $\delta -1.67$  ( $^1J(\text{PtH}) = 558 \text{ Hz}$  and a doublet splitting with  $J(^{13}\text{CH}) = 40 \text{ Hz}$  was also observed), and in the  $^{13}\text{C}$  NMR spectrum the carbonyl resonance was at  $\delta 191$  as a septet with  $^1J(\text{PtC}) = 434 \text{ Hz}$  [cf.  $\delta 209$ ,  $^1J(\text{PtC}) = 776 \text{ Hz}$  for **1**]<sup>18</sup> with the intensities expected for a  $\text{Pt}_3(\mu_3\text{-CO})$  group.<sup>12</sup> At room temperature only a broad resonance in the  $^{13}\text{C}$  NMR spectrum was observed at  $\delta 191$  without  $^{195}\text{Pt}$  satellites and the coupling of  $^{13}\text{C}$  to the  $\text{Pt}_3(\mu_3\text{-H})$  resonance in the  $^1\text{H}$  NMR was also lost. These data strongly indicate that reversible dissociation of CO from **2** occurs rapidly

(14) Migration of a proton through a triangle of metal atoms has been suggested to explain the reversible protonation of  $[\text{Ni}_{12}(\text{CO})_{21}][\text{H}_4\text{-n}]^{m-}$  in which the hydride ligands are interstitial and may also be involved in the protonation of  $[\text{Co}_6(\text{CO})_{15}]^{2-}$  and in the migration of hydrogen atoms through metallic lattices. This appears to be the first direct evidence and the first time that the barrier to inversion has been determined. The data do not rule out transition states with lower symmetry, for example, with hydride bridging one edge, but these are less likely. A complex with an almost planar  $\text{Er}_3(\mu\text{-H})$  group is known. Broach, R. W.; Dahl, L. F.; Longoni, G.; Chini, P.; Schulz, A. J.; Williams, J. M. *Adv. Chem. Ser.* 1978, 167, 93. Hart, D. W.; Teller, R. G.; Wei, C.-Y.; Bau, R.; Longoni, G.; Campanella, S.; Chini, P.; Koetzle, T. F. *Angew. Chem., Int. Ed. Engl.* 1979, 18, 80. Evans, W. J.; Meadows, J. H.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* 1982, 104, 2015.

(15) Puddephatt, R. J.; Azam, K. A.; Hill, R. H.; Brown, M. P.; Nelson, C. D.; Moulding, R. P.; Seddon, K. R.; Gossel, M. C. *J. Am. Chem. Soc.* 1983, 105, 5642. We note that if the Pt-Pt distance in **3** is the same as in **1** (2.6337 Å) the Pt-H distance in a planar  $\text{Pt}_3(\mu_3\text{-H})$  unit would be 1.52 Å, at the low end of the range of M-H bond lengths of 1.5-2.1 Å.<sup>16</sup> Of course the Pt-Pt distance might be greater in the transition state, and M-M bonds are usually longer when bridged by hydride ligands than when bridged by CO.

(16) Teller, R. G.; Bau, R. *Struct. Bonding (Berlin)* 1981, 44, 1. Chiang, M. Y.; Bau, R.; Minghetti, G.; Bandini, A. L.; Banditelli, G.; Koetzle, T. F. *Inorg. Chem.* 1984, 23, 124. Minghetti, G.; Bandini, A. L.; Banditelli, G.; Bonati, F.; Szostak, R.; Strouse, C. E.; Knobler, C. B.; Kesz, H. D. *Inorg. Chem.* 1983, 22, 2332.

(17) Mealli, C. *J. Am. Chem. Soc.* 1985, 107, 2245. We note that cyclopropane is protonated at an edge or corner, whereas  $[\text{Pt}_3(\mu\text{-dppm})_3]^+$  is protonated at the center. This difference could have been predicted from the different MO sequences in the two cases.

(18) The presence of a  $\mu_3\text{-CO}$  group in **2** is tentative at this stage. The NMR data show that, on the NMR time scale, the CO interacts equally with all Pt atoms, but the  $\nu(\text{CO})$  value is unprecedented for a  $\mu_3\text{-CO}$  group. The anomalous data can be rationalized in terms of an extremely weak  $\text{Pt}_3(\mu_3\text{-CO})$  bond or it is possible that the CO in **2** is terminal or semi triply bridging but fluxional even at  $-90^\circ\text{C}$ . **2** certainly represents the time-averaged structure. The remarkable changes in chemical shift and  $^1J(\text{PtH})$  coupling constant for the  $\text{Pt}_3(\mu_3\text{-H})$  resonance of **2** with temperature (vide infra) can be interpreted in terms of  $\sim 20\%$  "effective" dissociation of CO at room temperature, assuming that the NMR parameters of this proposed complex are similar to those of **3**.

at room temperature and at temperatures as low as  $-60^\circ\text{C}$ . However, the  $\text{CH}_2\text{P}_2$  resonance of the dppm ligands was an "AB" quartet [ $\delta(\text{CH}^a\text{H}^b)$  5.43, 5.07,  $^2J(\text{H}^a\text{H}^b) = 14 \text{ Hz}$ ] and samples containing both **2** and **3** gave separate, though broadened, NMR signals even at room temperature, showing that complete dissociation of the CO ligand from **2** is not fast on the NMR time scale. We suggest that effective reversible dissociation of the  $\text{Pt}_3(\mu_3\text{-CO})$  bond occurs rapidly at room temperature but that the CO remains within the cage of phenyl rings surrounding the  $\mu_3$ -site and escapes only slowly into solution.<sup>18</sup>

The reaction  $\mathbf{1} + \text{H}^- \rightarrow \mathbf{2} \rightleftharpoons \mathbf{3} + \text{CO}$  clearly defines a novel bimolecular mechanism of ligand substitution at the  $\mu_3$ -site, in which the intermediate **2** is sufficiently stable to be isolated.<sup>19</sup>

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(19) The electron configuration in **2** is analogous to that in  $[\text{Pt}_3(\mu_3\text{-SnCl}_3)_2(\text{cod})_3]$ .<sup>17</sup> However, when two different  $\mu_3$  ligands are present it seems that one is strongly and the other is weakly bound.<sup>8</sup> In complex **2**  $\text{H}^-$  binds more strongly than CO, and it is the CO that is weakly bound. The lower value of  $^1J(\text{PtH})$  also suggests a weaker PtH bond in **2** than in **3**. This mutual weakening of the bonds across the  $\text{Pt}_3$  triangle is analogous to the trans influence in mononuclear complexes.

### Photoelectron Spectra and Bonding in Cerocene, Bis( $\pi$ -[8]annulene)cerium(IV)

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Quasi-relativistic SCF- $X\alpha$  scattered-wave calculations have recently indicated that cerocene (bis( $\pi$ -[8]annulene)cerium(IV)) has an electronic structure unexpectedly similar to that of bis( $\pi$ -[8]annulene)uranium(IV) (uranocene) and -thorium(IV) (thorocene).<sup>1</sup> Various theoretical criteria indicate a substantial covalency for the lanthanide sandwich including a degree of f-orbital interaction comparable to uranocene itself.<sup>2</sup> Such involvement of 4f orbitals in ring-metal bonding in an organo-lanthanide compound would be unusual and unprecedented but the simple existence of cerocene should alone be considered to be remarkable: the compound combines a strong reducing agent (the [8]annulene dianion rings) with a powerful oxidizing agent, cerium(IV). This combination would imply that the structure could not be that of a simple ionic cluster. We have reproduced the synthesis of cerocene reported by Greco, Cesca, and Bertolini;<sup>3,4</sup>

(1) Rösch, N.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* 1983, 105, 7237.

(2) Rösch, N. *Inorg. Chim. Acta* 1984, 94, 297.

(3) Greco, A.; Cesca, S.; Bertolini, G. *J. Organomet. Chem.* 1976, 113, 321.

**Table I.** Ionization Energies of Cerocene

band label	ionization energy (IE), eV	$\Delta IE,^a$ eV	X $\alpha$ transition state energy, eV	X $\alpha$ $\Delta E,^{a,b}$ eV
a	6.75	0	6.31 ( $e_{2u}$ )	0
a'	(6.92) <sup>c</sup>			
b	7.68	0.93	7.20 ( $e_{2g}$ )	0.89
b'	(7.81) <sup>c</sup>			
c	9.98	3.23	9.42 ( $e_{1u}$ )	3.11
c'	(10.32) <sup>c</sup>	3.57	9.84 ( $e_{1g}$ )	3.53

<sup>a</sup>Difference compared to band a. <sup>b</sup>Reference 1. <sup>c</sup>Fine structure. Shoulders are in parentheses.

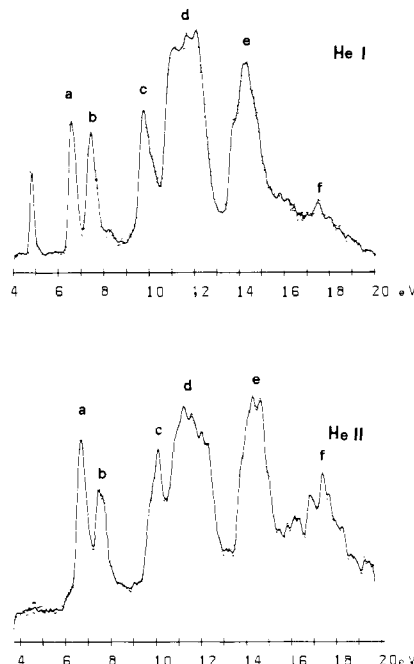
chemical properties and the photoelectron spectrum agree with the theory and suggest the importance of ring-metal covalency in this unusual compound.

The reaction of cerium(IV) isopropoxide with triethylaluminum in cyclooctatetraene gives the reported air-sensitive, brown-black microcrystalline compound. The compound shows a single signal in <sup>1</sup>H NMR at 5.9 ppm in THF-*d*<sub>8</sub> or at 5.75 ppm in toluene-*d*<sub>8</sub>. When the toluene solution of the complex was exposed to air, the brown solution became pale yellow and the <sup>1</sup>H NMR contained only one peak at 5.61 ppm, which is the resonance for neutral cyclooctatetraene. The infrared spectrum agrees with that reported. Conversion of bis([8]annulene)cerate(III)<sup>5</sup> ion to cerocene can be accomplished electrochemically. The reversible half-wave potential for the Ce(IV)/Ce(III) couple in this system is -1.28 V vs. NHE<sup>6</sup> and is, to our knowledge, the lowest Ce(IV)/Ce(III) couple reported.<sup>7</sup> This observation suggested that bis([8]-annulene)cerate(III) ion could be chemically converted to cerocene with mild oxidizing agents; indeed, we found that shaking a THF solution with excess silver iodide gives quantitative conversion to cerocene. This simple procedure is clearly the preparation of choice.

Cerocene reacts slowly with UCl<sub>4</sub> to give uranocene; this behavior is similar to that of thorocene and unlike the bis( $\pi$ -[8]-annulene)lanthanate(III) anions that react rapidly with UCl<sub>4</sub>. Cerocene also hydrolyzes in wet THF more slowly than thorocene to produce a mixture of 80% 1,3,5- and 20% 1,3,6-cyclooctatrienes.<sup>8</sup> This reactivity pattern does not suggest an ionic cluster.

Electronic absorption bands of thorocene at 2.75 eV and uranocene at 2.01 eV assigned as ligand-metal charge-transfer excitations,  $e_{2g}(\pi) \rightarrow e_{3u}(f)$ , agree well with the X $\alpha$  orbital energy differences, 3.03 and 1.97 eV, respectively. We now report that cerocene has an intense band ( $\epsilon \approx 8000$ ) at 469 nm (2.63 eV) in THF with a broad shoulder that, on deconvoluting using Gaussian functions,<sup>9</sup> has  $\lambda_{max}$  570 nm (2.18 eV,  $\epsilon \approx 1000$ ). The latter band is in good agreement with the calculated orbital energy difference of 1.92 eV.<sup>1,2</sup> We note that this band has comparable intensity to the visible band in uranocene ( $\epsilon = 1800$ ).

A further test of the theory is the direct comparison of the X $\alpha$  transition state energies with the ionization potentials determined from photoelectron spectra. The spectra were recorded on a Perkin-Elmer PS 18 spectrometer modified by the inclusion of a hollow cathode discharge source giving a high output of He(II) photons (Helectros Development Corp.). The spectra were run

**Figure 1.** Photoelectron spectrum of cerocene.

at 140 °C and "multiple scan mode" with the aid of a channeltron electron multiplier and a MOSTEK computer interfaced directly to the spectrometer. The results of 10 scans were averaged; the signal-to-noise ratio for the He(I) spectrum is greater than 10<sup>3</sup>. The energy scale of consecutive scans was locked to reference values of the Ar P<sub>3/2</sub> and He (1s<sup>-1</sup>) self-ionization lines.

The photoelectron spectra of cerocene (Figure 1) are similar to those of thorocene. There are two bands (a and b in Figure 1) in the 6–8-eV region; both show fine structure. A well-resolved band (c) is present in the 9–10-eV range (Table I). Some other rather overlapped structures (d–f) follow in the higher ionization energy region up to 19 eV. The bands present beyond 11 eV are common features of photoelectron spectra of all of the [8]annulene complexes thus far studied.<sup>10–13</sup> They belong to inner  $\pi$  and  $\sigma$  MO's having major contributions from the ligands. By analogy to the actinide compounds and on the basis of the X $\alpha$ -SW calculations, bands a and b are undoubtedly associated with ionization from the  $e_{2u}$  and  $e_{2g}$  MO's, respectively. The fine structure associated with these bands is probably due to vibronic Jahn-Teller effects in the ion states. Band c is taken to represent the ionizations from both the  $e_{1g}$  and  $e_{1u}$  MO's. This band shows a shoulder in the higher ionization energy side whose separation from the main peak compares well with the computed X $\alpha$ -SW  $e_{1u}$ - $e_{1g}$  splitting. The intensity changes in this band on going to He(II) radiation are comparable to those observed in the actinide series. The excellent agreement between the experimental and theoretical ionization potential differences (Table I) gives additional credence to the interpretation of the X $\alpha$  wave functions.<sup>1,2</sup>

The chemistry of organolanthanide compounds in the +2 and +3 oxidation states is that of essentially ionic systems; however, theory, reaction chemistry, and spectroscopy combine in the case of cerocene to show that this higher oxidation state organolanthanide has substantial ring-metal covalency and that metal 4f orbitals are involved in such bonding.

**Acknowledgment.** This work was supported in part by NATO Grant 1237. N.R. was supported by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie. The

(4) We have not been able to reproduce the synthesis of the compound reported with much different properties by: Kalsotra, B. L.; Multani, R. K.; Jain, B. D. *Chem. Ind. (London)* **1972**, 339.

(5) Hodgson, K.; Mares, F.; Starks, D.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 8650.

(6) In THF with tetrabutylammonium tetrafluoroborate as supporting electrolyte; the peak-to-peak separation by cyclic voltammetry was the same as for the ferrocene reference. We are indebted to K. Moran for technical assistance in this determination.

(7) We thank Professor K. Raymond for this observation.

(8) Unpublished results of Robert A. Moore.

(9) (a) We are indebted to Scott Gronert for this analysis. (b) A definite assignment of both bands is not possible at this time; however, measurements with substituted cerocenes in several solvents are currently in progress.

(10) Clark, J. P.; Green, J. C. *J. Chem. Soc., Dalton Trans.* **1977**, 305.

(11) Fragala, I.; Condorelli, G.; Zanella, P.; Tondello, E. *J. Organomet. Chem.* **1976**, *122*, 357.

(12) Bruno, G.; Ciliberto, E.; Fischer, R. D.; Fragala, I.; Spiegl, A. W. *Organometallics* **1982**, *1*, 1060.

(13) Green, J. C.; Payne, M. P.; Streitwieser, A., Jr. *Organometallics* **1983**, *2*, 1707.

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## Organo-Transition-Metal-Based Approach to the Synthesis of C-Glycosides

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Formation of a carbon-carbon bond at the anomeric center of a pyranoside or furanoside is a key transformation in the total synthesis of C-glycosides and polyether antibiotics.<sup>1</sup> Several methods have been developed to affect this transformation including sigmatropic rearrangements,<sup>2</sup> nucleophilic addition to glycols,<sup>3</sup> and addition of allylmetal derivatives to glycosyl derivatives.<sup>4</sup> Recently, organometallic based approaches to the preparation of C-glycosides have been reported.<sup>5</sup> In this paper, we report the stereoselective preparation of glycosylmanganese pentacarbonyl complexes. Carbonylation of these complexes with retention of configuration and subsequent ligand incorporation into the acylmanganese bond results in the formation of C-glycosides. The overall transformation replaces the anomeric bromide by an acyl residue in a highly stereoselective fashion (see Scheme I).<sup>6</sup> This approach to the synthesis of C-glycosides is especially appealing because the acyl residue can carry a diversity of functional groups (see Scheme II).

Glycosyl bromides **1-5**<sup>7</sup> react with sodium pentacarbonylmanganate(I)<sup>8</sup> (**6**) in THF at -78 °C to give stable glycosyl-

Scheme I

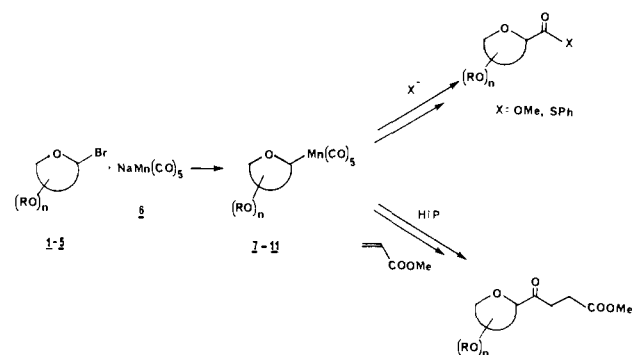


Table I. Preparation of Glycosyl Manganese Pentacarbonyl Complexes

glycosyl bromide	manganese complex	yield, %
 <b>1a</b> : R = Me <b>1b</b> : R = Bn	 <b>7a</b> : R = Me <b>7b</b> : R = Bn	75
		75
		60
		65
		70

manganese pentacarbonyl complexes **7-11** in good yield (Table I). The displacement occurred with equal facility in either the pyranosyl or furanosyl series and displayed excellent stereoselectivity.  $\alpha$ -Bromides **1**<sup>7</sup> and **2**<sup>7</sup> reacted with inversion of configuration to produce exclusively  $\beta$ -manganese complexes **7**<sup>9</sup> and **8**<sup>9</sup>, respectively. The stereochemistry of the glycosyl complex **7a** was determined by <sup>1</sup>H NMR analysis. The C-1 proton appeared as a doublet at  $\delta$  3.94 with  $J = 10.2$  Hz and indicated an axial proton.<sup>10</sup> Alternatively, the stereochemistry at the anomeric center could be determined by subsequent transformations of the complexes (vide infra). Mannosyl bromide **3**<sup>7</sup> gave a 1:2 mixture of

(8) Prepared by reduction of  $Mn_2(CO)_{10}$ , according to the procedure of Darenbourg: Drew, D.; Darenbourg, M. Y.; Darenbourg, D. J. *J. Organomet. Chem.* **1975**, *85*, 73.

(9) All compounds gave satisfactory IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, MS, and elemental analytical data.

(10) Jackman, L. M.; Sternhell, S. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed.; Pergamon Press: Oxford, 1969; pp 280-298.

(1) For an excellent review of this topic, see: Hanessian, S. "Total Synthesis of Natural Products: The 'Chiron' Approach"; Pergamon Press: New York, 1983.

(2) Ireland, R. E.; Thaisrivongs, S.; Vanier, N.; Wilcox, C. S. *J. Org. Chem.* **1980**, *45*, 48. Ireland, R. E.; McGarvey, G. J.; Anderson, R. C.; Badond, R.; Fitzsimmons, B.; Thaisrivongs, S. *J. Am. Chem. Soc.* **1980**, *102*, 6178. Curran, C. P.; Suh, Y.-G. *Ibid.* **1984**, *106*, 5002 and references cited therein.

(3) Dawe, R. D.; Fraser-Reid, B. *J. Chem. Soc., Chem. Commun.* **1981**, 1180.

(4) Posner, G. H.; Haines, S. R. *Tetrahedron Lett.* **1985**, *26*, 1823. Keck, G. E.; Enholm, E. J.; Kachensky, D. F. *Ibid.* **1984**, *25*, 1867. Hosomi, A.; Sakata, Y.; Sakurai, H. *Ibid.* **1984**, *25*, 2383. Kunz, H.; Weissmuller, J.; Muller, B. *Ibid.* **1984**, *25*, 3571. Kozikowski, A. P.; Sorgi, K. L. *Ibid.* **1984**, *25*, 2085. Wilcox, C. S.; Long, G. W.; Suh, H. *Ibid.* **1984**, *25*, 395. Hanessian, S.; Sato, K.; Liak, T. J.; Danh, N.; Dixit, D.; Cheney, B. V. *J. Am. Chem. Soc.* **1984**, *106*, 6114. Nicholau, K. C.; Dolle, R. E.; Chucholowski, A.; Randall, J. L. *J. Chem. Soc., Chem. Commun.* **1984**, 1153.

(5) For an excellent review of the application of the Oxo reaction to carbohydrate chemistry, see: Rosenthal, A. *Adv. Carbohydr. Chem.* **1968**, *23*, 59. See also: Trainor, G. L.; Smart, B. E. *J. Org. Chem.* **1983**, *48*, 2447. Dunkerton, L. V.; Serino, A. J. *J. Org. Chem.* **1982**, *47*, 2812. Arai, I.; Daves, G. D., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 287. Arai, I.; Lee T. D.; Hanna, R.; Daves, G. D., Jr. *Organometallics* **1982**, *1*, 742.

(6) We have reported the use of alkylmanganese pentacarbonyl complexes for the preparation of a variety of functional groups; see: (a) DeShong, P.; Slough, G. A. *Organometallics* **1984**, *3*, 636. (b) DeShong, P.; Slough, G. A. *J. Am. Chem. Soc.*, submitted for publication.

(7) Glycosyl bromides **1-5** were prepared from the corresponding protected 1-*p*-nitrobenzoates: Plessars, N. R.; Goldstein, I. *J. Carbohydr. Res.* **1981**, *89*, 211. Koto, S.; Morishima, N.; Miyata, Y.; Zen, S. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2639. Barker, R.; Fletcher, H. G., Jr. *J. Org. Chem.* **1961**, *26*, 4605.