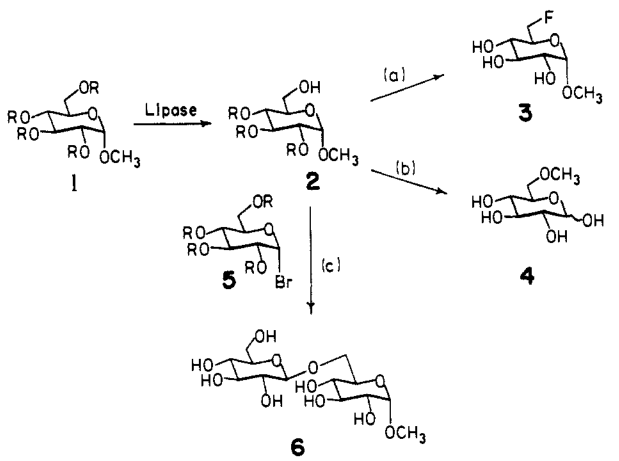
Scheme I. Enzymatic and Chemical Synthesis of Sugar Derivatives[a]



[a] (a) 1, DAST; 2, CH_3ONa (catalytic)/CH_3OH. (b) 1, CH_2N_2; 2, CH_3ONa (catalytic)/CH_3OH; 3, H^+. (c) 1, CF_3SO_3Ag; 2, CH_3ONa (catalytic)/CH_3OH. R = acetyl for **1a**, **2a**, and **5a**, pentanoyl for **1b** and **2b**, and octanoyl for 1c and **2c**.

Of different acyl sugars tested, the octanoyl derivatives are the best substrates but for technical consideration the pentanoyl derivatives are the best to work with.[6] The sugar derivatives with 6-OH functionality prepared in this study are useful synthons in carbohydrate chemistry. The glucose derivatives, for example, can be converted chemically to other useful compounds such as methyl 6-deoxy-6-fluoro-α-D-glucopyranoside (**3**)[7] and 6-*O*-methyl-D-glucose (**4**)[8] and the disaccharide methyl 6-*O*-β-D-glucopyranosyl-α-D-glucopyranoside (**6**).[9] We compare this enzymatic procedure with the existing methods[2,3] and conclude that the lipase-catalyzed reactions offer a better process for the synthesis of 6-substituted or 6-modified hexopyranoses. In addition to the α-D-glucosides, the β-derivatives and the other sugars including D-galactose and D-mannose derivatives containing the same protecting groups are good substrates for the enzyme and deacylated selectively at the primary hydroxyl positions.[6,10]

The regioselectivity observed in the hydrolytic reactions indicates that the reverse reactions, i.e., esterification of free sugars, may also be regioselective. An attempted esterification of methyl glucoside with pentanoic acid in hexane using the *Candida* lipase, however, showed only little reaction (2–3%), probably due to the poor solubility of substrate in the organic solvent. Acylation of free sugars via transesterification using the enzyme also resulted in a poor yield, and the products were not isolated. The transesterification, however, did work when pancreatic lipase was used in the presence of isopropenyl acetate as acyl donor. The detailed procedures will be published separately.

In a representative procedure for the preparation of **2b**, compound **1b** (0.48 g, 1 mmol) was dissolved in acetone (1 mL) and added to 10 mL of phosphate buffer (0.1 M, pH 7) containing $CaCl_2$ (3 mM) and NaCl (0.2 M). Lipase (10 mg from Sigma) was added and the reaction mixture was stirred at room temperature and titrated automatically with NaOH (0.02 M) to keep the mixture at pH 7. After 3 days the suspension was extracted with $CHCl_3$ (3 × 40 mL) and the organic layer dried over $MgSO_4$. After evaporation of the solvent, the residue was purified by silica gel column chromatography (ether/hexane = 1/1, v/v) to give 0.41 g of **2b** as a syrup; yield 90%; $[\alpha]^{22}_{\mathrm{D}}$ +98.2° (*c* 0.55, $CHCl_3$). Analysis of the product with NMR indicates that the 6-position is specifically deacylated.[9] By increasing each component proportionally, a 50-mmol-scale preparation has been carried out and the results are essentially the same as those in small-scale preparations. The free OH group of **2b** was replaced with F by reaction with (diethylamino)sulfur trifluoride (DAST)[11] to give the F-derivative which upon deacylation with CH_3ONa (catalytic)/CH_3OH[12] gave **3** in 56% yield based on **2b**: mp 102–104 °C, $[\alpha]^{22}_{\mathrm{D}}$ +146° (*c* 1.0, H_2O) [lit.[11] mp 102–104 °C, $[\alpha]^{25}_{\mathrm{D}}$ +148.6° (*c* 1, H_2O)]. Treatment of **2b** with CH_2N_2 followed by deacylation and acid hydrolysis gave **4** in 60% overall yield: mp 147–149 °C (EtOH/EtOAc), $[\alpha]^{25}_{\mathrm{D}}$ +56° (*c* 1, H_2O). The NMR data are consistent with those reported.[8]

Acknowledgment. Support of this research by the National Science Foundation (CHE 8318217) and the Searle Scholars Program is gratefully acknowledged.

Supplementary Material Available: Experimental details for the preparation of compounds **1–4**, galactose and mannose derivatives, and physical constants (^1H and ^{13}C NMR data, melting points, and specific rotations) (6 pages). Ordering information is given on any current masthead page.

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[6] We have tested acetyl, pentanoyl, and octanoyl derivatives of D-glucose and pentanoyl derivatives of D-mannose and D-galactose. The octanoyl derivatives cause emulsion when extracted with organic solvents. The acetyl derivatives are not substrates for the enzyme. The pentanoyl glucopyranoside derivative is hydrolyzed by the enzyme with a specific activity of 30 units/g, compared to 250 units/g with the octanoyl derivatives. The α-form is hydrolyzed 5 times as fast as the β form (1 unit = 1 μmol of substrate hydrolyzed per min. The enzyme cost is $50/100 g).

[7] 6-Deoxy-6-fluoro-D-glucose is an antitumor reagent: Bessel, E. M.; Courtenay, V. D.; Foster, A. B.; Jones, M.; Westwood, J. H. *Eur. J. Cancer* **1973**, *9*, 463. For chemical synthesis of this compound, see: Sharma, M.; Korytnk, W. *Tetrahedron Lett.* **1977**, *6*, 573. Reference 10.

[8] Useful for the study of Maillard reaction and Amadori transformations: Cleve, J. W. V.; Inglett, G. E.; Tjarks, L. W. *Carbohydr. Res.* **1985**, *137*, 259.

[9] Forsgren, M.; Jansson, P. E.; Kenne, L. *J. Chem. Soc., Perkin Trans 1* **1985**, 2383–2388.

[10] Determined by ^1H and ^{13}C NMR analysis. The protons at C-6 shift 0.6–0.8 ppm upfield after deacylation. The ^{13}C NMR spectrum reveals a 0.7–1 ppm upfield shift after deacylation. Yoshimoto, K.; Itatani, Y.; Tsuda, Y. *Chem. Pharm. Bull.* **1980**, *28*, 2065.

[11] Card, P. J.; Reddy, G. S. *J. Org. Chem.* **1983**, *48*, 4734.

[12] Vogel, A. *Practical Organic Chemistry*, 3rd ed.; Longman: London and New York, 1978; p 460.

Reactive Chromium Methylidene Cations: Intramolecular Migration of Methylene from Chromium into a C–H Bond of the Cyclopentadienyl Ligand

John L. Hubbard* and William K. McVicar

Department of Chemistry, University of Vermont
Burlington, Vermont 05405

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While considerable attention has been directed to the study of cationic alkyidene complexes $(\eta\text{-}C_5R_5)MLL'\text{–}CH_2^+$ (M = Fe, Ru; L, L′ = CO, PR_3; M = Re, L = NO, R′ = PR_3),[1] there has been no report of isoelectronic $(\eta\text{-}C_5R_5)M(NO)_2\text{–}CH_2^+$ analogues (M = Cr, Mo, W). We report here a facile, high-yield synthesis of the $CpCr(NO)_2\text{–}CH_2X$ complexes (Cp = $\eta\text{-}C_5H_5$, $\eta\text{-}C_5H_4CH_3$, $\eta\text{-}C_5(CH_3)_5$; X = Cl, Br) which serve as precursors for generating the $(\eta\text{-}C_5R_5)Cr(NO)_2\text{–}CH_2^+$ species upon halide abstraction.[2] Remarkably, the methylidene cation complexes produced in such a manner from $(\eta\text{-}C_5H_5)Cr(NO)_2\text{–}CH_2X$ and $(\eta\text{-}C_5H_4\text{–}CH_3)\text{-}Cr(NO)_2\text{–}CH_2X$ directly undergo an unprecedented rearrange-

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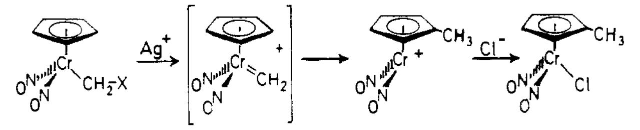
[1] (a) Davison, A.; Krussell, W.; Michaelson, R. *J. Organomet. Chem.* **1974**, *72*, C7. (b) Brookhart, M.; Studabaker, W. B.; Husk, G. R. *Organometallics* **1985**, *4*, 943 and references therein. (c) Jolly, P. W.; Pettit, R. *J. Am. Chem. Soc.* **1966**, *88*, 5044. (d) Moss, J. R.; Pelling, S. *J. Organomet. Chem.* **1982**, *236*, 221. (e) Pelling, S.; Botha, C.; Moss, J. R. *J. Chem. Soc., Dalton Trans.* **1983**, 1495. (f) King, R. B.; Braitsch, D. M. *J. Organomet. Chem.* **1973**, *54*, 9. (g) Green, M. L. H.; Ishaq, M.; Whiteley, R. N. *J. Chem. Soc. A* **1967**, 1580. (h) Nelson, G. O. *Organometallics* **1983**, *2*, 1474. (i) Kao, S. C.; Lu, P. P. Y.; Pettit, R. *Organometallics* **1982**, *1*, 911. (j) Gladysz, J. A.; Knobler, C. B.; Strouse, C. E.; Patton, A. T. *J. Am. Chem. Soc.* **1983**, *105*, 5804 and references therein.

[2] Piper and Wilkinson (Piper; Wilkinson *J. Inorg. Nucl. Chem.* **1956**, *3*, 104) reported the synthesis of $(\eta\text{-}C_5H_5)Cr(NO)_2\text{–}CH_2Cl$ in 3% yield, but their partial characterization (IR) deviates significantly from our fully characterized material.

0002-7863/86/1508-6422$01.50/0

Scheme I



ment, where the methylene moiety has migrated into a C–H bond of the cyclopentadienyl ring.

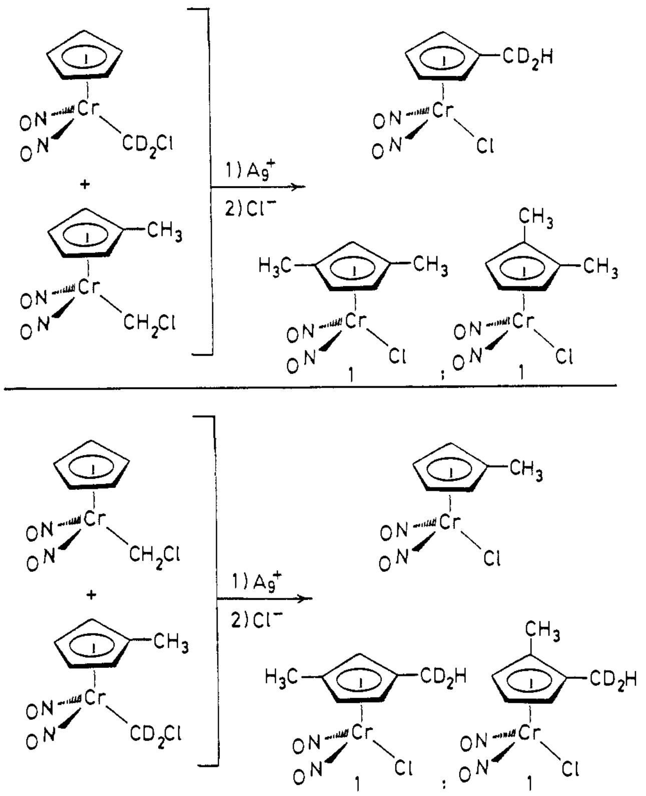
Addition of ethereal diazomethane to a dilute ether solution of $(\eta\text{-}C_5H_5)Cr(NO)_2Cl$[3] (25 °C, 1 h) in the presence of Cu powder cleanly gives $(\eta\text{-}C_5H_5)Cr(NO)_2\text{–}CH_2Cl$ as air-stable green crystals in 88% yield after workup.[4] The $(\eta\text{-}C_5H_5)Cr(NO)_2\text{–}CH_2Br$, $(\eta\text{-}C_5H_4CH_3)Cr(NO)_2\text{–}CH_2X$, and $(\eta\text{-}C_5(CH_3)_5)Cr(NO)_2\text{–}CH_2X$ analogues (X = Cl, Br) are obtained in a similar fashion.[5] No reaction between the metal halide and diazomethane occurs in the absence of Cu powder.

Reaction of $(\eta\text{-}C_5H_5)Cr(NO)_2\text{–}CH_2Cl$ with $AgBF_4$ in CH_2Cl_2 at room temperature gives a product identified by ^1H NMR as the $(\eta\text{-}C_5H_4(CH_3))Cr(NO)_2^+$ cation,[6] where the methylene moiety has been inserted into a C–H bond of the $(\eta\text{-}C_5H_5)$ ring (Scheme I).

Migration of a metal-bound methylene unit into a C–H bond of a coordinated $(\eta\text{-}C_5H_5)$ ring has never been observed from similar treatment of any haloethyl transition-metal complexes with Ag^+.[7] Treatment of analogous $(\eta\text{-}C_5H_5)Fe(CO)_2\text{–}CH_2X$ complexes with Ag^+ results in significant intermolecular methylene transfer to cyclohexene.[1c] For $(\eta\text{-}C_5H_5)Cr(NO)_2\text{–}CH_2X$ and $(\eta\text{-}C_5H_4(CH_3))Cr(NO)_2\text{–}CH_2X$, no cyclopropanation products are ever detected in the reaction mixture when halide abstraction is performed in the presence of cyclohexene. In the case of $(\eta\text{-}C_5(CH_3)_5)Cr(NO)_2\text{–}CH_2Cl$, a small amount (ca. 5% yield) of norcarane is produced. Interestingly, no tetramethylethyl Cp products are detected in the halide abstraction from the $(\eta\text{-}C_5(CH_3)_5)Cr(NO)_2\text{–}CH_2X$ precursors, demonstrating the insertion process to be selective to sp^2 C–H bonds on the Cp ring.

The nature of the methylene migration reaction is further illuminated by deuterium labeling experiments. Treatment of a 1:1 mixture of either $(\eta\text{-}C_5H_5)Cr(NO)_2\text{–}CD_2Cl$ and $(\eta\text{-}C_5H_4(CH_3))Cr(NO)_2\text{–}CH_2Cl$ or $(\eta\text{-}C_5H_5)Cr(NO)_2\text{–}CH_2Cl$ and $(\eta\text{-}C_5H_4(CH_3))Cr(NO)_2\text{–}CD_2Cl$ with a stoichiometric amount of $AgBF_4$ in CH_2Cl_2 followed by addition of Cl^- (PPNCl or $HCl_{(g)}$) and then standard workup provides neutral Cr–Cl derivatives (Scheme II).[8] The results of both reactions show the production of methylene insertion products in >80% yields with no measurable crossover. This indicates an efficient methylene insertion process that could be described as an intramolecular attack on the Cp ring by an electrophilic methylene ligand.[9] The dimethylcyclopentadienyl products, readily identified by 270-MHz ^1H NMR, appear in a nearly equal distribution between 1,2- and 1,3-ring substitution.

Scheme II



Treatment of $(\eta\text{-}C_5H_5)Cr(NO)_2\text{–}CH_2X$ with AgOTs in CH_2Cl_2 gives $(\eta\text{-}C_5H_5)Cr(NO)_2\text{–}CH_2OTs$ in 82% yield.[10] The tosylate derivative reacts with ethereal HBF_4 or trifluoroacetic acid in CH_2Cl_2 (25 °C, 0.5 h) to cleanly give methylene insertion products analogous to those obtained by halide abstraction. This shows that the presence of Ag^+ is not necessary for the methylene migratory insertion.

In summary, the production of the new (halomethyl)chromium complexes as precursors for cationic methylidene complexes has permitted the documentation of a new form of transition-metal–methylidene reactivity, quite unlike the chemistry from closely related isoelectronic species. The underlying cause for this intramolecular reactivity is likely to revolve around the extremely strong π-withdrawing power of the two nitrosyl ligands working together as described by Hall.[11] This may have important catalytic implications for controlling reactions where a methylene

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[3] Hoyano, J. K.; Legzdins, P.; Malito, J. T. *Inorg. Synth.* **1978**, *18*, 126.

[4] (a) Best results are obtained when ca. 1 M ethereal CH_2N_2 (**Caution!** Toxic, possible explosion danger; see: *Aldrichimica Acta* **1983**, *16* (1), 3) is added slowly (0.5 mL/min) to ca. 15 mM ether solutions of the metal halides. Reaction progress is monitored by IR until starting material is consumed. Following a fast filtration through a plug of alumina I and removal of the ether in vacuo, the complexes are recrystallized from pure hexane at −45 °C. (b) $(\eta\text{-}C_5H_5)Cr(NO)_2CH_2Cl$: Anal. ($C_6H_7N_2O_2CrCl$) C, H, N; ^1H NMR (270 MHz, $CDCl_3$) δ 5.52 (s, 5 H,Cp), 4.26 (s, 2 H, CH_2); $^{13}C\{^1H\}$ (67.9 MHz, $CDCl_3$) δ 100.4 (Cp), 45.1 (CH_2); IR (KBr) ν_{NO} 1788 vs, 1675 vs cm^{-1}; MS (CI, isobutane) $[M]^+$ 3%, $[M - Cl]^+$ 100%, $[M - NO]^+$ 12%, $[M - CH_2Cl]^+$ 31%.

[5] (a) $(\eta\text{-}C_5H_4(CH_3))Cr(NO)_2CH_2Cl$: Anal. ($C_7H_9N_2O_2CrCl$) C, H, N; ^1H NMR (270 MHz, $CDCl_3$) δ 5.36 (t, 2 H, Cp), 5.28 (t, 2 H, Cp), 4.22 (s, 2 H, CH_2), 2.00 (s, 3 H, CH_3); $^{13}C\{^1H\}$ NMR (67.9 MHz, $CDCl_3$) δ 115.6 (Cp CH_3), 100.1, 100.0 (Cp), 45.9 (CH_2), 12.6 (CH_3); IR (KBr) ν_{NO} 1783 vs, 1676 vs cm^{-1}; MS (CI, CH_4) $[M]^+$ 4%, $[M - Cl]^+$ 100%, $[M - NO]^+$ 20%, $[M - CH_2Cl]^+$ 24%. (b) $(\eta\text{-}C_5(CH_3)_5)Cr(NO)_2CH_2Cl$: Anal. ($C_{11}H_{17}N_2O_2CrCl$) C, H, N; ^1H NMR (270 MHz, $CDCl_3$) δ 3.84 (s, 2 H, CH_2), 1.78 (s, 15 H, $C_5(CH_3)_5$); $^{13}C\{^1H\}$ NMR (67.9 MHz, $CDCl_3$) δ 109.0 (Cp), 50.6 (CH_2), 9.1 (CH_3); IR (KBr) ν_{NO} 1762 vs, 1658 vs cm^{-1}; MS (CI, isobutane) $[M]^+$ 1%, $[M - Cl]^+$ 100%, $[M - NO]^+$ 20%, $[M - CH_2Cl]$ 3%. (c) $(\eta\text{-}C_5H_5)Cr(NO)_2CH_2Br$: Anal. ($C_6H_7N_2O_2BrCr$) C, H, N; ^1H NMR (270 MHz, $CDCl_3$) δ 5.52 (s, 5 H, Cp), 4.02 (s, 2 H, CH_2); IR (KBr) ν_{NO} 1788 vs, 1674 vs cm^{-1}. (d) $(\eta\text{-}C_5(CH_3)_5)Cr(NO)_2CH_2Br$: Anal. ($C_{11}H_{17}N_2O_2BrCr$) C, H, N; ^1H NMR (270 MHz, $CDCl_3$) δ 3.6 (s, 2 H, CH_2), 1.77 (s, 15 H, $C_5(CH_3)_5$); IR (KBr) ν_{NO} 1789 vs, 1675 vs cm^{-1}.

[6] ^1H NMR shows the production of the cation is >90% yield in CD_2Cl_2. The cation was independently prepared by Cl^- abstraction from $(\eta\text{-}C_5H_4CH_3)Cr(NO)_2Cl$; see, for details on the chemistry of these cations: Wojcicki; Regina *Inorg. Chem.* **1980**, *19*, 3803.

[7] See H. Werner's review for aspects of half-sandwich halomethyl chemistry: Werner, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 927–949.

[8] (a) Both reactions were run to ensure that methyl substitution on the Cp ring did not affect the results. Deuterated complexes were prepared by using CD_2N_2 (isotopic enrichment ca. 90% as determined by ^1H NMR). (b) $(\eta\text{-}C_5H_3(CH_3)_2)Cr(NO)_2Cl$: Anal. (mixture of isomers, $C_7H_9N_2O_2CrCl$) C, H, N; ^1H NMR for 1,2-Me_2Cp isomer (270 MHz, $CDCl_3$) δ 5.38 (t, 1 H (H_a on Cp 4-position)), 5.31 (d, 2 H (H_b,H_b' on the Cp 3,5-positions)) $J_{ab} = 3$ Hz; 1.91 (s, 6 H, CH_3 ring substituents) for the 1,3-Me_2Cp isomer, 5.21 (d, 2 H (H_a, H_a' on the Cp 4,5-positions)), 5.07 (m, 1 H, (H_b on the Cp 2-position)), 1.98 (s, 6 H, CH_3 ring substituents); IR (CH_2Cl_2) 1801 vs, 1694 vs cm^{-1}.

[9] Intramolecular electrophilic attack by a metal-bound carbene on a phenyl ring of a triphenylphosphine, resulting in *displacement* of a phenyl hydrogen atom has been observed; see: Roper; et al. *J. Chem. Soc., Chem. Commun.* **1984**, 1000.

[10] $(\eta\text{-}C_5H_5)Cr(NO)_2CH_2(SO_3C_7H_7)$: Anal. ($C_{13}H_{14}N_2O_5SCr$) C, H, N; ^1H NMR (270 MHz, $CDCl_3$) δ 7.75 (d, 2 H, C_6H_4), 7.30 (d, 2 H, C_6H_4), 5.47 (s, 5 H, Cp), 5.04 (s, 2 H, CH_2), 2.41 (s, 3 H, CH_3); IR (KBr) ν_{NO} 1793 vs, 1675 vs cm^{-1}.

[11] Hall, M, B.; Kolthammer, B. W. S.; Morris-Sherwood, B. J. *Inorg. Chem.* **1981**, *20*, 2771.

fragment becomes joined to another unsaturated ligand in the coordination sphere of a transition-metal atom.

Acknowledgment. We acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, and a University of Vermont Institutional Grant for support of this work.

Synthesis of $(Me_3P)_2Ni(CH_2CMe_2\text{-}o\text{-}C_6H_4)$ and Its Reactivity toward CO_2, CO, and CH_2O. First Observation of a Carbonyl-Carbonate Oxidative Conproportionation Mediated by a Transition-Metal Complex

Ernesto Carmona,* Pilar Palma, Margarita Paneque, and Manuel L. Poveda*

Departamento de Química Inorgânica
Facultad de Química, Universidad de Sevilla
41012 Sevilla, Spain

Enrique Gutiérrez-Puebla* and Angeles Monge

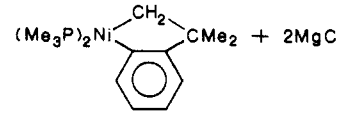
Instituto de Química Inorgânica Elhûyar
C.S.I.C. Serrano 113, 28006 Madrid, Spain
Departamento de Química Inorgânica
Facultad de Química, Universidad Complutense
28040 Madrid, Spain

Received April 14, 1986

The insertion of small molecules into transition-metal–carbon bonds plays a prominent role in a number of important stoichiometric and catalytic processes. Among these reactions, those involving carbon monoxide have been extensively studied[1] both from a synthetic and a mechanistic point of view. Less well-studied, although of increasing interest,[2] are the insertions of carbon dioxide, while only a few examples of formaldehyde insertion[3] have been reported to date. In this paper we wish to report our findings on the insertion chemistry and related reactions of these molecules with the nickelacyclopentene[4] complex $(Me_3P)_2Ni(CH_2CMe_2\text{-}o\text{-}C_6H_4)$ (**1**). The reactions studied are summarized in Scheme I.

Complex **1** is formed in good yields[5] by the reaction of $NiCl_2(PMe_3)_2$ with 2 equiv of $Mg(CH_2CMe_2Ph)Cl$, *in the presence of traces of I^-* (eq 1).

$$NiCl_2(PMe_3)_2 + 2Mg(CH_2CMe_2Ph)Cl \xrightarrow{I^-}$$



$+ 2MgCl_2$ (1)

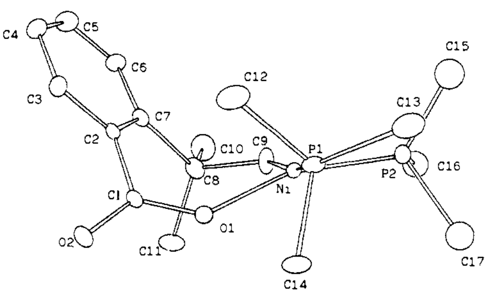
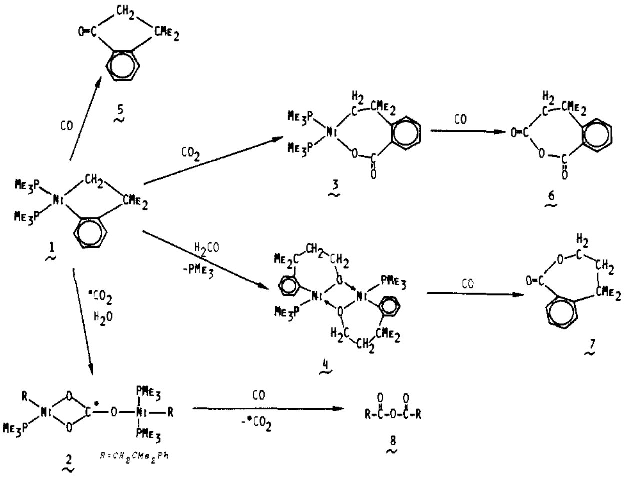


Figure 1. ORTEP diagram for **3** and atom labeling scheme. Important bond distances and angles: Ni–P1 = 2.291 (4), Ni–P2 = 2.143 (4), Ni–O1 = 1.877 (9), Ni–C9 = 1.96 (1) Å; C1–O1–Ni = 137.4 (9)°.

Scheme I



A number of experimental observations made during the progress of this work indicate[6] a catalytic role for I^-, but no mechanistic information on this intringuing reaction is yet available. Although **1** does not react with water under normal conditions, a fast protolytic cleavage of the Ni–aryl carbon bond takes places in the presence of wet CO_2, with quantitative formation[9] of the dimetallic carbonate **2**, which contains a $\mu_2\text{-}\eta^1,\eta^2\text{-}CO_3$ bridge (eq 2). This coordination mode of the bridging carbonate ligand has some precedents in the literature.[11] If the reaction with carbon dioxide is carried out under very strict anhydrous conditions, the yellow nickelalactone **3**, i.e., the normal

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[1] Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980. Casey, C. P.; Baltusis, L. M. *J. Am. Chem. Soc.* **1982**, *104*, 6347. Jablonski, C. R.; Wang, Y. *Inorg. Chem.* **1982**, *21*, 4037. Berke, H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 7224.

[2] Darensbourg, D. J.; Hanckel, R. K.; Bauch, C. G.; Pala, M.; Simmons, D.; White, J. N. *J. Am. Chem. Soc.* **1985**, *107*, 7463. Darensbourg, D. J.; Grötsch, G. *J. Am. Chem. Soc.* **1985**, *107*, 7473.

[3] (a) Tikkanen, W. R.; Pettersen, J. L. *Organometallics* **1984**, *3*, 1651. (b) Maatta, E. A.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 3576. (c) Leoni, P.; Pasquali, M. *J. Organomet. Chem.* **1983**, *255*, C31.

[4] A related nickelabenzocyclopentene complex has been recently obtained via a different route: Bennett, M. A.; Hambley, T. W.; Roberts, N. K.; Robertson, G. B. *Organometallics* **1985**, *4*, 1992.

[5] A cold (–70 °C) stirred suspension of $NiCl_2(PMe_3)_2$ (1.68 g, ca. 6 mmol) in 70 mL of Et_2O was treated with $Mg(CH_2CMe_2Ph)Cl$ (15.4 mL of a ca. 0.78 M Et_2O solution) in the presence of MgI_2 (two drops of a ca. 7×10^{-2} M Et_2O solution). After 2 h of stirring at room temperature and following normal workup, complex 1 can be crystallized as orange prisms from Et_2O or petroleum solutions in ca. 75% yield. If the activation of Mg during the Grignard synthesis is accomplished by addition of I_2, no additional I^- is required for the metalation reaction to take place.

[6] In the absence of I^-, only the monoalkyl $NiCl(CH_2CMe_2Ph)(PMe_3)_2$[7] is formed. The cyclometalated complex 1 cannot be detected even after stirring for 24 h at room temperature in the presence of 2–3 equiv of the Grignard reagent. It is possible that free I^- accelerates the second alkylation to give the unobserved $Ni(CH_2CMe_2Ph)_2(PMe_3)_2$ which readily undergoes a δ-elimination[8] reaction to produce 1. The intermediacy of a dialkylnickel(II) species is supported by the observation that $Ni(CH_2CMe_2Ph)_2$ (tmed)[7] reacts with PMe_3 to give complex 1. We are unaware of any previous report of a such dramatic influence of traces of I^- in the behavior of a Grignard reagent.

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[9] Three drops of water were added to a solution of 1 in Et_2O (0.96 g, ca. 2.8 mmol; 25 mL), and the mixture was pressurized with CO_2 (3 atm). Stirring at room temperature for ca. 15 min and evaporation to dryness furnished yellow microcrystalline **2** in almost quantitative yield. Recrystallization from Et_2O at –20 °C gives analytically pure crystals of **2** in ca. 90% yield. Representative spectroscopic data for **2**: $^{31}P\{^1H\}$ NMR (C_6D_6, 21 °C) δ –3.8 (br s, P_A) and –17.3 (br s, P_B); $^{13}C\{^1H\}$ NMR (C_6D_6, 21 °C) δ 12.3 (br s, PMe_3), 18.0 (v br, $Ni\mathit{C}H_2CMe_2$), 32.5 (s, $CH_2C\mathit{Me}_2Ph$), 41.0 (s, $CH_2\mathit{C}Me_2Ph$), 124.6, 126.5, 127.7 (s, *C*-H Ar), 154.1 (br s, quaternary aromatic carbon), 170.4 (s, CO_3). An exchange process of the PMe_3 ligands probably similar to that observed in a related Rh system[10] could be responsible for the simplicity of the observed spectra. IR (Nujol mull) CO_3 absorption at 1505 cm^{-1}. Anal. Calcd for $C_{30}H_{53}O_3P_3Ni_2$: C, 53.6; H, 7.9; O, 7.1. Found: C, 53.5; H, 7.7; O, 7.9. The Me_3SiCH_2 analogue of **2** has been structurally characterized: Marin, J. M., unpublished results.

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