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Formates in methanol synthesis? The reversible production of methyl formate from coordinated formate

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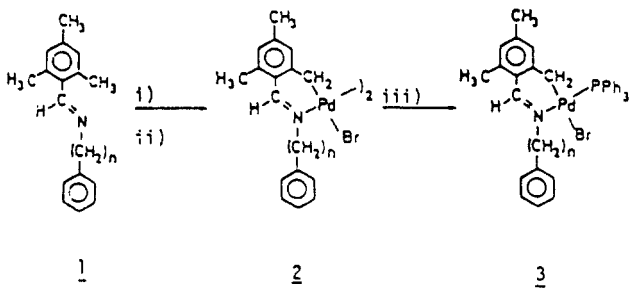
Scheme I[a]



[a] **a** (n = 0); **b** (n = 1); **c** (n = 2). (i) $Pd(AcO)_2$, $MeCO_2H$, reflux, 1 h and 30 min; (ii) LiBr, EtOH, reflux, 30 min; (iii) PPh_3, $(Me)_2CO$, reflux, 45 min.

methylnaphthalene, only accomplish metalation of the peri-carbon atom of the naphthyl group with formation of a six-membered ring, even when a five- or six-membered ring with Pd–C(sp^3) bonds would have resulted if the metalation had taken place at the methyl groups. These results illustrate the easier cleavage of aromatic C–H bonds as compared to aliphatic C–H bonds, as has been confirmed recently by Crabtree.[5]

The action of $Pd(AcO)_2$ on the amines 2,4,6-$(CH_3)_3C_6H_2CH{=}N(CH_2)_nC_6H_5$ (n = 0, 1, or 2) in anhydrous acetic acid has been examined (see Scheme I).

These imines permit a simultaneous comparison of the metalation tendency of the sp^3- or sp^2-carbon atoms and the importance of the number of members of the ring formed. Thus, metalation of the ortho-methyl groups gives six-membered rings, while the metalation of the ortho-phenyl carbons would give cyclometalated species with four-, five-, or six-membered rings, for n = 0, 1, or 2, respectively.

In the three cases, metalation of an ortho-methyl group with formation of a six-membered metallacycle takes place (ca. 70% yield). These results are specially remarkable for n = 1, since the metalation of the aromatic ortho carbon should yield a five-membered ring.

The novel cyclopalladated compounds **3** were unambiguously characterized by analytical and spectroscopic data.[6] The structure of **3a**[7] was confirmed by an X-ray crystallographic study.

The crystal structure of **3a** (Figure 1) consists of discrete molecules linked by van der Waals' forces. The Pd atom

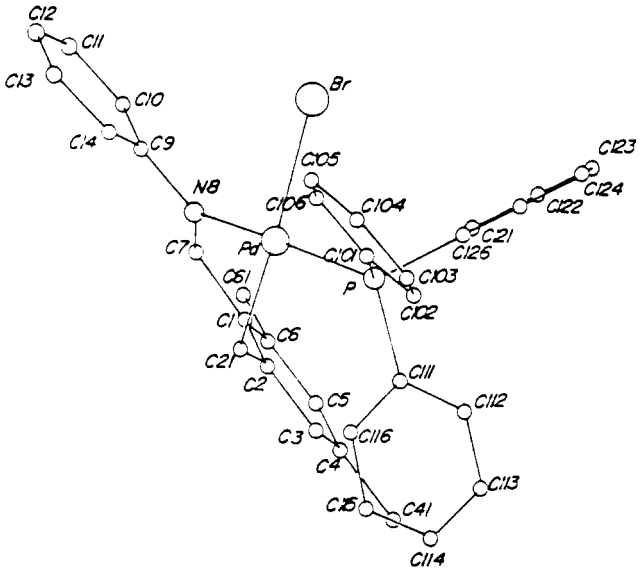


Figure 1. Molecular structure of **3a**. Important bond lengths (Å) and angles (deg): Pd–Br, 2.553 (1); Pd–N(8), 2.138 (4); Pd–C(21), 2.060 (5); Pd–P, 2.258 (1); C(21)–C(2), 1.483 (9); C(2)–C(1), 1.422 (8); C(1)–C(7), 1.460 (8); C(7)–N(8), 1.275 (8) Å; N(8)–Pd–Br, 90.8 (1); C(21)–Pd–N(8), 82.2 (2); P–Pd–Br, 93.1 (1); P–Pd–C(21), 93.9 (2); C(21)–Pd–Br, 172.9 (2); P–Pd–N(8) 169.6 (1); Pd–C(21)–C(2), 104.3 (4); C(21)–C(2)–C(1), 121.1 (5); C(2)–C(1)–C(7), 118.1 (5); C(1)–C(7)–N(8), 126.2 (5); C(7)–N(8)–Pd, 118.3 (4)°.

displays a distorted square-planar geometry but with usual bond lengths and angles around the metal. The bonding of C(21) and N(8) with the Pd atom causes the torsion of the C(1)–C(7) (31.8 (6)°) and N(8)–C(9) (−37.1 (6)°) bonds, which gives the C_4NPd six-membered ring, a half-skew-chair conformation with the Pd atom out of the plane (−1.325 Å).[8]

These results show that the original assumption, that metal ions preferring square-planar geometry favor five-membered ring, is unnecessarily limiting since a six-membered ring can also accommodate a central metal in a square-planar geometry as has been reported before.[3b,c]

Supplementary Material Available: Tables of anisotropic parameters, fractional coordinates, bond lengths, and bond angles (5 pages); a listing of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

(5) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245.

(6) Complexes gave satisfactory elemental analyses. ^{1}H NMR in $CDCl_3$ (coupling constants in Hz): **3a**, δ 8.20 (d, $^4J_{P-H}$ = 12.7, 1 H, HC=N–), 7.77–7.24 (br, 20 H, PPh_3 and C_6H_5–), 6.66 (s, 1 H, ar), 5.60 (s, 1 H, ar), 2.87 (d, $^3J_{P-H}$ = 5.1, 2 H, CH_2Pd), 2.36 (s, 3 H, CH_3), 2.05 (s, 3 H, CH_3); **3b**, δ 8.18 (d, $^4J_{P-H}$ = 13.0, 1 H, HC=N–), 7.84–7.25 (br, 20 H, PPh_3 and C_6H_5–), 6.66 (s, 1 H, ar), 5.60 (br s, 3 H, CH_2N, and 1 H, ar), 2.35 (d, $^3J_{P-H}$ = 4.9, 2 H, CH_2Pd), 2.32 (s, 3 H, CH_3), 2.03 (s, 3 H, CH_3); **3c**, δ 7.92 (d, $^4J_{P-H}$ = 12.1, 1 H, HC=N–), 7.76–7.25 (br, 20 H, PPh_3 and C_6H_5–), 6.61 (s, 1 H, ar), 5.60 (s, 1 H, ar), 4.64 (br t, 2 H, NCH_2), 3.42 (t, 2 H, $C_6H_5CH_2$), 2.53 (d, $^3J_{P-H}$ = 5.4, 2 H, CH_2Pd), 2.24 (s, 3 H, CH_3), 2.03 (s, 3 H, CH_3).

(7) Crystal data: $C_{34}H_{29}NPBrPd$; M_r 668.9; monoclinic; a = 14.763 (2) Å, b = 19.525 (3) Å, c = 9.966 (1) Å; β = 90.81°; V = 2881 (1) Å^3, D_{calcd} = 1.54 g cm^{-3}; space group $P2_1/n$; Z = 4; $F(000)$ = 1104; λ(Mo Kα) = 0.71069 Å; μ(Mo Kα) = 21.82 cm^{-1}; room temperature; crystal dimensions 0.15 × 0.15 × 0.15 mm; Philips PW-1100 four-circle diffractometer; graphite-monochromatized Mo Kα radiation; ω-scan technique; scan width 1°; scan speed 0.03 deg s^{-1}; three reflections were measured every 2 h as orientation and intensity control; significant intensity decay was not observed; 4263 reflections in the range $2 < \theta < 25°$; 3850 observed [$I > 2.5\sigma(I)$]. The structure was solved by direct methods (MULTAN). The structure was refined by full-matrix square-planar method, using the SHELX76 computer program. The function minimized was $w|(F_o) - (F_c)|^2$, where $w = |\sigma^2(F_o) + 0.001(F_o)^2|^{-1}$. A total of 26 hydrogen atoms were obtained by a difference synthesis and refined with an overall isotropic temperature factor, while the remaining atoms were refined anisotropically. The final R was 0.041 (R_w = 0.044) for all observed reflections.

(8) The deviations from the mean plane are as follows: N(8), −0.168; C(7), 0.207; C(1), −0.042; C(2), −0.113; C(21), 0.116 Å.

Formates in Methanol Synthesis? The Reversible Production of Methyl Formate from Coordinated Formate

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Summary: The disproportionation of trimethylsilyl formate to methyl formate, carbon dioxide, and hexamethyldisiloxane is shown to be experimentally reversible and has been investigated in both the forward and reverse

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Table I. Disproportionation of Trimethylsilyl Formate[a]

temp, °C	time, h	$[Me_3SiO_2CH]_i$, M	$[Me_3SiO_2CH]_f$, M	$[Me_6Si_2O]$, M	$[HCO_2CH_3]$, mM	H_2, mmol	CO, mmol	CO_2, mmol
250	25	1.54	0.05	0.74	57	72	70	129
210	187	1.43	0.32	0.57	30	39	40	60
180	139	1.40	0.85	0.29	5	5	15	8

[a] Reaction of Me_3SiO_2CH in dioxane with a total volume of 140 mL. Products analyzed by gas chromatography as described in the supplementary material.

directions, yielding an equilibrium constant of $K = 8.9 \times 10^6$ atm^2 M^{-1} at 250 °C in dioxane solution. Furthermore, the product of interest, methanol, results from a slower decarbonylation reaction of the initial methyl formate product.

Despite extensive progress in synthetic organometallic chemistry, several fundamental reaction processes relevant to commercial C_1 chemistry still remain exclusively within the domain of heterogeneous surface catalysis. One such area has been the reaction chemistry of surface formate to yield organic products.[1] Thus, surface formate is a common component produced on metal oxide catalysts upon exposure to either the reactants, synthesis gas,[2,3] or the products, methanol[4] or formaldehyde.[5] Furthermore, surface formate has been proposed as a key intermediate in methanol synthesis on metal oxide catalysts.[2] As a first step to developing this unique area of formate chemistry under homogeneous conditions, we have recently shown that alkali-metal formates can, indeed, be rapidly disproportionated when slurried with various metal oxides to yield methanol[6] at rates[7] up to 5.5 mol·(CH_3OH) Kg^{-1} (cat.) h^{-1} with lead oxide catalyst at 230 °C according to the stoichiometry in eq 1 by a mechanism postulated to include

$$4HCO_2^- \rightarrow CH_3OH + CO + 2CO_3^{2-} \quad (1)$$

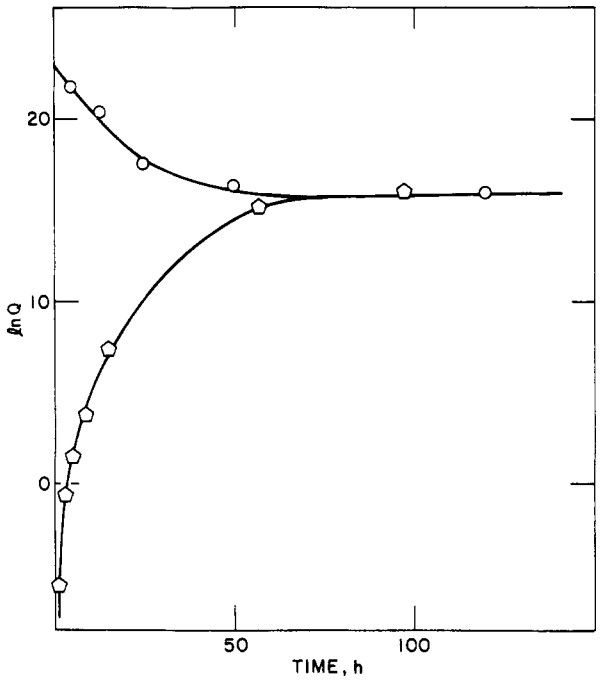

Figure 1. The natural logarithm of the experimental reaction quotients, $Q = [HCO_2CH_3][Me_6Si_2O]^2P_{CO_2}{}^2/[Me_3SiO_2CH]^4$, vs. time in 1,4-dioxane at 250 °C: ⬡, $[Me_3SiO_2CH]_i$ = 1.46 M; ○, $[HCO_2CH_3]_i$ = 2.69 M, $[Me_6Si_2O]_i$ = 0.52 M.

ketonic decarboxylation,[9] Tischenko dimerization,[10] and the decarbonylation of methyl formate[11] as given in eq 2–4, respectively. Unfortunately, kinetic confirmation of this

$$2HCO_2^- \rightarrow CH_2{=}O + CO_3^{2-} \quad (2)$$

$$2CH_2{=}O \rightarrow HCO_2CH_3 \quad (3)$$

$$HCO_2CH_3 \rightarrow CH_3OH + CO \quad (4)$$

reaction scheme has been hampered due to the heterogeneous conditions inherent to the use of metal oxide catalysts. We report here the first homogeneous disproportionation of formate (eq 5) with the resolution of the important mechanistic criterion that methyl formate is produced prior to methanol as required by eq 3 and 4.

$$4Me_3SiO_2CH \rightleftharpoons HCO_2CH_3 + 2CO_2 + 2Me_6Si_2O \quad (5)$$

The thermolysis of trimethylsilyl formate in dioxane solvent proceeds smoothly to yield methyl formate and hexamethyldisiloxane as the initial liquid products; see Table I.[12] Furthermore, labeled methyl-d_3 formate-d is

(1) For comparison to solution formate chemistry see: Darensbourg, D. J.; Kudaroski, R. A. *Adv. Organomet. Chem.* **1983**, *22*, 129. Panessa, R. S.; Trogler, W. C. *J. Am. Chem. Soc.* **1982**, *104*, 3529. Ford, P. C. *Acc. Chem. Res.* **1981**, *14*, 31. King, A. D., Jr.; King, R. B.; Yang, D. B. *J. Am. Chem. Soc.* **1981**, *103*, 2699. Strauss, S. H.; Whitmire, K. H.; Schriver, D. F. *J. Organomet. Chem.* **1979**, *174*, C59. Volpin, M. E.; Kolmnikov, I. S. *Organomet. React.* **1975**, *5*, 313.

(2) Surface formate in the hydrogenation of CO: Edwards, J. F.; Schrader, G. L. *J. Catal.* **1985**, *94*, 175. He, M.-Y.; Ekerdt, J. G. *Prepr.—Am. Chem. Soc., Div. Pet. Chem.* **1984**, *29*, 532. Akhter, S.; Chen, W. H.; Lui, K.; Kung, H. H. *J. Catal.* **1984**, *85*, 437. Klier, K. In *Catalysis on the Energy Scene*; Kaliaguine, S.; Mahay, A., Ed.; Elsevier Science Publishers B. V.: Amsterdam, 1984; p 439. Deluzarche, A.; Kieffer, R.; Muth, A. *Tetrahedron Lett.* **1977**, 3357.

(3) Surface formate in the hydrogenation of CO_2: Deluzarche, A.; Cressely, J.; Kieffer, R. *J. Chem. Res., Synop.* **1979**, 136; *J. Chem. Res., Miniprint* **1979**, 1657. Solymosi, F.; Erdohelyi, A.; Kocsis, M. *J. Catal.* **1980**, *65*, 428. Solymosi, F.; Erdohelyi, A.; Bansagi, T. *J. Chem. Soc., Faraday Trans.* **1981**, *77*, 2645. Ramarson, E.; Kieffer, R.; Kiennemann, A. *J. Chem. Soc., Chem. Commun.* **1982**, 645.

(4) Surface formate in the decomposition of CH_3OH: Kagel, R. O. *J. Phys. Chem.* **1967**, *71*, 844. Kagel, R. O.; Greenler, R. G. *J. Chem. Phys.* **1968**, *49*, 1638. Ueno, A.; Onishi, T.; Tamaru, K. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 2652. Ueno, A.; Onishi, T.; Tamaru, K. *Trans. Faraday Soc.* **1971**, *67*, 3585. Hertl, W.; Cuenca, A. M. *J. Phys. Chem.* **1973**, *77*, 1120. Bowker, M.; Houghtow, H.; Waugh, K. C. *J. Chem. Soc., Faraday Trans.* **1981**, *77*, 3023. Yamashita, K.; Naito, S.; Tamaru, K. *J. Catal.* **1985**, *94*, 353.

(5) Surface formate in the reactions of $CH_2{=}O$: Stuve, E.; Madix, R. J. *Surf. Sci.* **1982**, *119*, 279. Groff, R. P.; Manogue, W. H. *J. Catal.* **1983**, *79*, 462.

(6) Klingler, R. J.; Rathke, J. W. *J. Am. Chem. Soc.* **1984**, *106*, 7650. Klingler, R. J.; Rathke, J. W. *Prepr.—Am. Chem. Soc., Div. Pet. Chem.* **1984**, *29*, 596.

(7) For comparison, typical values reported[8] with commercial methanol synthesis catalysts operating under standard conditions range from 9.3 mol Kg^{-1} h^{-1} at 250 °C to 150 mol Kg^{-1} h^{-1} at 270 °C.

(8) Herman, R. G.; Klier, K.; Simmons, G. W.; Finn, B. P.; Bulko, J. B.; Kobylinski, T. B. *J. Catal.* **1979**, *56*, 407.

(9) March, J. *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*; McGraw-Hill: New York, 1968; p 370.

(10) Reference 9, p 910. Mamoru, A. *J. Catal.* **1983**, *83*, 141.

(11) Stahler, A. *Chem. Ber.* **1914**, *47*, 580.

(12) The simple mixture of light gases in columns 7–9 completes the stoichiometric balance. Transient quantities of CH_2O, Me_3SiH, and tentatively identified $(Me_3SiO)_2CH_2$ are observed.[13]

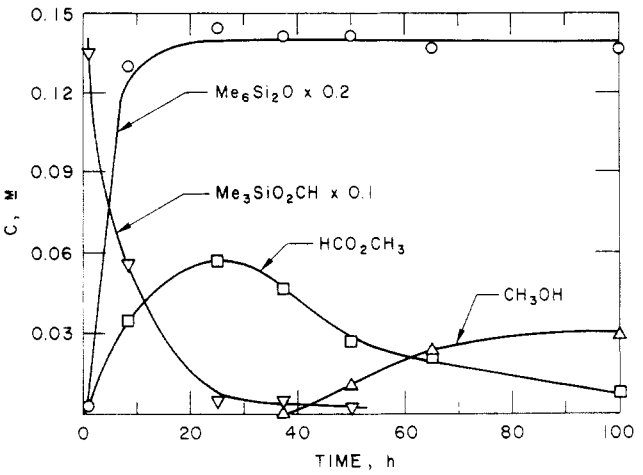

Figure 2. Time dependence of the liquid products for the disproportionation of trimethylsilyl formate at 250 °C in 1,4-dioxane.

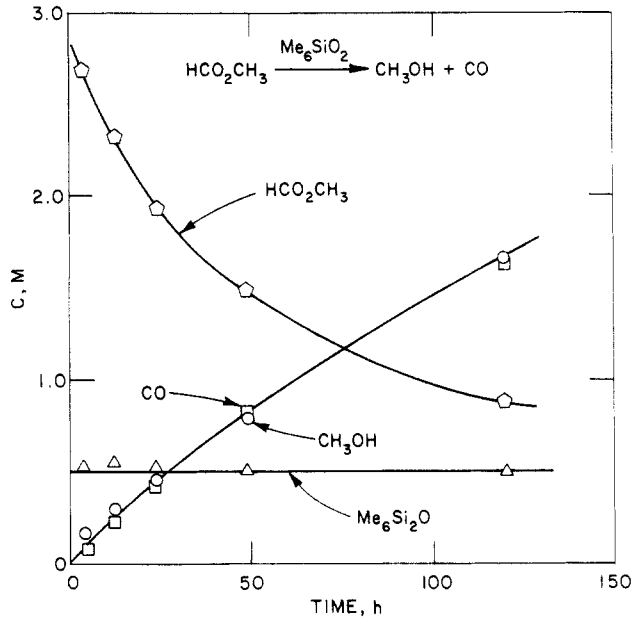

Figure 3. Decarbonylation of methyl formate with Me_6Si_2O in dioxane at 250 °C.

isolated[13] from the thermolysis of trimethylsilyl formate-*d*, thereby demonstrating that the formate moiety is the source of the hydrogen in the methyl formate product. Significantly, the process described by eq 5 is experimentally reversible at 250 °C in dioxane. Thus, the same equilibrium reaction quotient is obtained in Figure 1 starting with either pure trimethylsilyl formate (pentagons) or a mixture of methyl formate and hexamethyldisiloxane (circles). Continued heating of the solution in the first row of Table I (under the gas mixture of columns 7–9) for an additional 75 h at 250 °C reveals a second slower process that results in the production of methanol, which reaches a concentration of 30 mM, at the expense of methyl formate, whose concentration declines to 8 mM as indicated in Figure 2. Indeed, it is possible to independently demonstrate that the decarbonylation of methyl formate (eq 4) under these experimental conditions (Figure 3) is slow in comparison to the initial formate disproportionation of eq 5 (Table I). Significantly, the results in Figure 2 clearly demonstrate that methyl formate is produced prior to methanol in the homogeneous trialkylsilyl system. In contrast, previous results under heterogeneous conditions were ambiguous because they yielded mixtures consisting of methanol together with smaller quantities of methyl formate.[6]

It is hoped that further analysis of this homogeneous formate system may provide a useful comparison to the reaction chemistry of surface formate being studied on heterogeneous methanol synthesis catalysts[2] and the parallel surface formate chemistry being investigated on the heterogeneous catalyst for the oxidation of methanol to formaldehyde.[5]

Acknowledgment. We thank Professor J. Halpern for helpful discussions. Support for this work was provided by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy.

Supplementary Material Available: Experimental details for the thermolysis of trimethylsilyl formate (6 pages). Ordering information is given on any current masthead page.

(13) Experimental details together with the ^2H and ^{13}C NMR spectrum of the isolated methyl-d_3 formate-*d* are given in the supplementary material. Also included are representative first-order rate plots for formate ion decay which exhibits a deuterium kinetic isotope effect of 2.0.

Nucleophilic Acylation of Metal Carbonyls: Synthesis and Structure of a Tetracarbonyl(pivaloylacyl)ferrate and Its Reaction with Electrophiles[1]

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Summary: The nucleophilic acylation of pentacarbonyliron by in situ generated pivaloyllithium at low temperature affords an acylferrate complex. The structure of the $[(Ph_3P)_2N]^+$ salt is determined by X-ray analysis. The acylferrate reacts with electrophiles to give thermolabile products which are characterized as tetracarbonyl acylcarbene complexes by IR spectroscopy.

The tandem addition of a nucleophile and an electrophile across the C–O bond of metal carbonyls represents the most versatile access to transition-metal carbene complexes.[2] In general, organolithium reagents are used as

(1) Reactions of Complex Ligands, Part 28. For part 27, see: Dötz, K. H.; Sturm, W. *J. Organomet. Chem.*, in press.

(2) Recent review: Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, 1983.

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