bent towards the triphenylene by approximately 11–15°. As a consequence, the proximal NH protons are directed towards the aromatic plane rather than the caffeine molecule and interact only weakly. The distance between the coplanar aromatic surfaces is 3.42 Å which is optimal for a donor–acceptor interaction. It turned out to be impossible to accomplish the crystallization of this receptor with sidechains shorter than *n*-hexyl. The hexyl groups must be packed in the crystal and, indeed, two of them save space by folding in, while the third alkyl chain breaks the symmetry and produces a preferred directionality. Disordered caffeine was not observed. We were even able to localize the hydrogen atoms involved in hydrogen bonding.[14] The values found are in the typical ranges.

In conclusion, rigid functionalized triketals of hexahydroxytriphenylene open up the opportunity to generate novel receptors for the selective recognition of alkylated oxopurines. For caffeine, the bonding interaction can be observed directly. Together with the results from X-ray crystallography, a consistent picture of the receptor's guest binding features evolves.

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[8] All new compounds were obtained pure (elemental analysis (C, H, N) within ±0.4 %).

[9] Compound **2**: mp 198 °C; ^1H NMR (600 MHz, CD_2Cl_2, 25 °C, TMS): $\delta = 0.78$ (t, $^3J_{H,H} = 7$ Hz, 9 H, CH_3), 1.06–1.18 (m, 24 H), 1.64–1.73 (m, 12 H), 2.12–2.31 (m, 21 H), 2.78–2.88 (m, 12 H), 4.51 (br., 3 H, N–H distal), 4.71 (s, 3 H, N–H proximal), 7.82 (s, 6 H, triphenylene); ^{13}C NMR (150.8 MHz, CD_2Cl_2, 25 °C, TMS): $\delta = 14.15$, 21.45, 22.91, 26.94, 28.68, 30.44, 31.89, 34.77, 38.51, 40.51, 57.77, 101.94, 122.37, 124.97, 147.97, 157.85.

[10] The binding constants were obtained by fitting the titration curves with the Specfit program package: Specfit v.2.12, Spectrum Software Associates, Chapel Hill, NC, USA; H. Gampp, M. Maeder, C. J. Meyer, A. D. Zuberbühler, *Talanta* **1986**, *33*, 943, and references therein. The given error is systematical; multiple determination demonstrated an excellent reproducibility of the binding constants. A low mean variation is observed in the determined values.

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[13] X-ray crystal structure analysis of **2** with caffeine: $C_{74}H_{100}N_{10}O_{11} \cdot 3.5\,CH_3OH$, $M_r = 1417.79$, light yellow crystal, 0.50 × 0.35 × 0.25 mm^3, $a = 13.596(1)$, $b = 13.794(1)$, $c = 22.979(1)$ Å, $\alpha = 80.09(1)$, $\beta = 82.40(1)$, $\gamma = 67.41(1)^\circ$, $Z = 2$, $V = 3909.2(4)$ $Å^3$, $\rho_{calcd} = 1.204\ g\,cm^{-3}$, $\mu = 0.83\ cm^{-1}$, absorption correction with SORTAV ($0.971 \leq T \leq 0.992$), triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 22410 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.59\ Å^{-1}$, 13700 independent ($R_{int} = 0.033$) and 8862 observed reflections $[I \geq 2\sigma(I)]$, 911 refined parameters, $R = 0.094$, $wR^2 = 0.267$, max. (min.) residual electron density was $1.09(-0.69)\ e\,Å^{-3}$ close to the disordered solvate molecules, disorder refined with constraints, hydrogens calculated at the nitrogen atoms from difference fourier calculations, others calculated and refined as riding atoms. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-139021. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Calcium-Catalyzed Selective and Quantitative Transformation of CH_4 and CO into Acetic Acid**

Mohammad Asadullah, Tsugio Kitamura,
and Yuzo Fujiwara*

Methane and ethane have exerted a profound economic and sociologic influence on the world at large because of their enormous reserves.[1] However, the use of methane in the direct synthesis of functionalized products is limited by the low reactivity of methane and poor product selectivity.[2] The search for new routes of methane transformation constituted an important field of research over the last two decades.[3] Carboxylation of methane with CO to afford acetic acid is an important functionalization process that is not industrially feasible at present. In 1992 we reported the Pd-catalyzed carboxylation of methane with CO in the presence of $K_2S_2O_8$ and CF_3COOH (TFA).[4] Recently we found that systems using a $Yb(OAc)_3/Mn(OAc)_2/NaClO/H_2O$ catalyst[5] and $Mg/K_2S_2O_8$/TFA promoter[6] cause the carboxylation of methane to give acetic acid. Magic-acid-induced[7] and $RhCl_3$-catalyzed[8] reactions of methane with CO were also developed. However, these processes have several practical drawbacks, such as low yield, cost of catalyst, and product selectivity. Herein we report almost quantitative carboxylation of methane with CO to afford acetic acid (**1**) with one of the cheapest chemicals, namely, $CaCl_2$, as catalyst.

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Our reaction of saturated hydrocarbons with CO in which Mg powder is used as a promoter[6] prompted us to investigate alkaline earth metal compounds as catalysts for the reaction of methane with CO (Table 1). In the absence of catalyst, no **1** was observed by GC analysis of the reaction mixture (entry 1), and this confirmed that the autoclave wall was not involved in the reaction of methane with CO to give any product. Addition of a catalytic amount of $CaCl_2$ gave **1** (entry 2). The other Ca compounds (entries 3–7) gave very low yields of **1**.

Table 1. Effect of calcium compounds on the carboxylation of methane with CO.[a]

Entry	Alkaline earth compound	Yield [mmol][b]	Yield [%][c]	TON[d]
1	none	trace	–	–
2	$CaCl_2 \cdot 2H_2O$	1.05	7.1	2.1
3	CaO	0.07	0.5	0.14
4	$CaCO_3$	0.04	0.3	0.08
5	$Ca(OAc)_2 \cdot 2H_2O$	0.04	0.3	0.08
6	$[Ca(acac)_2] \cdot 2H_2O$[e]	0.03	0.2	0.06
7	$Ca(OH)_2$	0.01	0.1	0.02
8	$CaSO_4 \cdot 2H_2O$	trace	–	–

[a] 25-mL autoclave, methane (20 atm, 15 mmol), CO (30 atm), calcium compound (0.5 mmol), $K_2S_2O_8$ (5 mmol), and TFA (5 mL) at 80 °C for 15 h. [b] Determined by GC. [c] Based on methane. [d] Based on the amount of Ca. [e] acac = acetylacetonate.

The optimization of the reaction conditions is summarized in Table 2. Experiments were conducted to gain insight into the reaction conditions that would favor the formation of **1** from methane and CO. Methane reacted at temperatures as low as 60 °C in moderate yield (entry 1). Increasing the temperature increases the yield of **1**, which is highest at 85 °C (entry 2). Temperature above 85 °C resulted in low yields. In the absence of CO the reaction did not give **1** but afforded 0.2 mmol of methyl trifluoroacetate (**2**). In this case methane is first oxidized to methanol, which then reacts with TFA to yield **2**. The reaction performed under an atmospheric pressure of CO gave a low yield of **1** (entry 3). Increasing the CO pressure resulted in an increase in the yield of **1** up to 50 atm, which gave the highest yield of **1** (1.54 mmol, entry 5). In this system CO acts as a trapping agent for the methyl radical to form the acetyl radical, which forms the acetic acid in this reaction. The reaction order with respect to CO partial pressure up to 20 atm was unity. However, it became fractional beyond 20 atm of CO.

Table 2. Effect of reaction conditions on the carboxylation of methane.[a]

Entry	*T* [°C]	CO [atm]	$K_2S_2O_8$ [mmol]	TFA [mL]	Methane [atm]	$CaCl_2$ [mmol]	Time *t* [h]	Yield [mmol][b]	Yield [%][c]
1	60	30	5	6	20	0.5	15	0.41	2.8
2	85	30	5	6	20	0.5	15	1.21	8.5
3	85	1	5	6	20	0.5	15	0.08	0.6
4	85	40	5	6	20	0.5	15	1.43	10.1
5	85	50	5	6	20	0.5	15	1.54	10.8
6	85	40	10	6	20	0.5	15	1.55	10.8
7	85	40	10	3	20	0.5	15	1.27	7.6
8	85	40	10	5	20	0.5	15	1.61	10.6
9	85	40	10	5	1	0.5	15	0.16	21.1
10	85	40	10	5	5	0.5	15	0.97	25.7
11	85	40	10	5	30	0.5	15	1.87	8.2
12	85	40	10	5	20	0.05	15	0.01	0.1
13	85	40	10	5	20	0.1	15	0.51	3.6
14	85	40	10	5	20	1	15	0.86	6.1
15	85	30	5	5	2	0.5	140[d]	1.52	93.8
16	85	40	10	5	30	0.1	200	3.05	13.5

[a] 25-mL autoclave. [b] GC yield. [c] Based on methane. [d] 2 mmol of TFAA was used.

The use of 10 mmol of $K_2S_2O_8$ resulted in a slightly higher yield than with 5 mmol (Table 2, entry 6). The number of moles of **1** formed increased up to 5 mL of TFA (entry 8). The effect of trifluoroacetic anhydride (TFAA) in the reaction mixture was also examined, and a positive effect was found with an optimum at 2 mmol of TFAA. The water of the catalyst quantitatively reacts with TFAA to give TFA. The reaction mixture thus becomes water-free, and production of **1** is improved. The use of solvents other than TFA was also investigated. Acetonitrile results in the same product distribution with significant yield (0.83 mmol), although there is an approximately twofold decrease in the amount of product formed after 15 h reaction time relative to TFA. To avoid the complexity of product analysis arising from an acetic acid solvent, ethane was used as substrate, and 0.24 mmol of propionic acid was obtained. In the case where water was used as the solvent, NaClO and H_2O_2 were used as oxidants, and lower activity was observed. No activity of the catalyst for the formation of **1** was observed in dichloromethane or 1,2-dichloroethane. Interestingly, methane underwent the reaction at atmospheric pressure and gave 21.1 % yield based on methane after 15 h (Table 2, entry 9). However, high methane pressures resulted in higher yields (1.87 mmol, entry 11). A first-order dependence of reaction rate on methane partial pressure was observed up to 5 atm. Amounts of catalyst smaller than 0.05 mmol did not give **1**. The reaction of methane with CO to give **1** is best catalyzed by 0.5 mmol of $CaCl_2$ (8.2 % yield; entry 11). Larger amounts of $CaCl_2$ also resulted in low yield (entry 14). The parameter with the largest effect was duration of the reaction. The product **1** is first observed after 2 h, after which its yield constantly increases with time. The catalyst did not lose activity even after 200 h when 0.1 mmol of $CaCl_2$ and 30 atm of methane were used, and the turnover number (TON) of the catalyst was 30.5. Selectivity for the acetic acid product in the liquid phase remained at 100 % during the entire course of the experiment. The best result was obtained with 2 atm of methane, 30 atm of CO, 0.5 mmol of $CaCl_2$, 5 mmol of $K_2S_2O_8$, 5 mL of TFA, and 2 mmol of TFAA. The reaction under these conditions gives almost quantitative yield (93.8 %, based on methane) after 140 h.[9]

We assume that the reaction proceeds through the formation of radicals ($CaO^{\bullet}$, $CH_3^{\bullet}$, and $CH_3CO^{\bullet}$). To confirm this assumption various types of radical scavengers, such as 2,4,6-tri-*tert*-butylphenol, tetrachloro-*p*-benzoquinone, and 2,2,6,6-tetramethylpiperidine, were added to the reaction mixture, and only traces or zero yield of **1** was obtained. This means that the reaction proceeds through the formation of radicals, which were trapped by the scavengers. The control reactions of ^{13}C-labeled methane with ordinary CO and of ^{13}C-labeled CO with ordinary methane were performed to investigate the actual source of the methyl and carbonyl groups of **1** and to elucidate the reaction path. From the ^{13}C NMR spectra of both the reaction mixtures it can be seen that except for two quartets of the TFA solvent, only singlet peaks are present at $\delta = 19.4$ (Figure 1a) and 182.3 (Figure 1b), and these are assigned to the $^{13}CH_3$ and $^{13}C{=}O$ groups of **1**, respectively. These facts confirm that the methyl and carbonyl groups of **1** are derived from $^{13}CH_4$ and ^{13}CO, respectively, and the selectivity for **1** is around 100%.

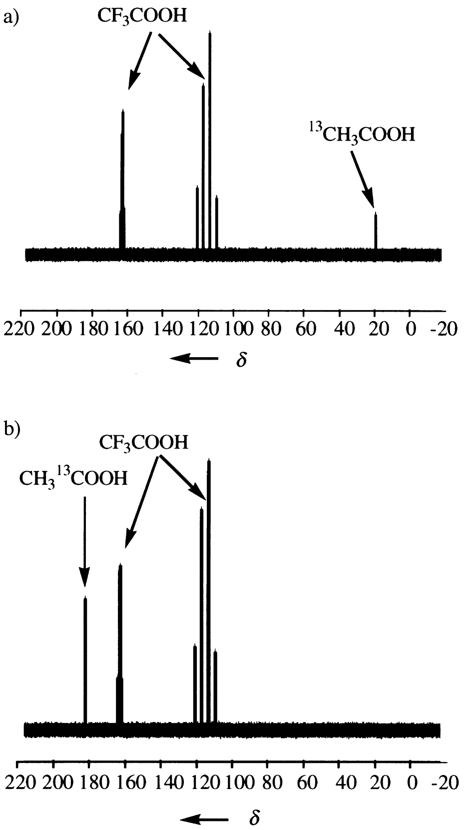

Figure 1. ^{13}C NMR spectra of the reaction mixtures after the reaction of $^{13}CH_4$ with CO (a) and of CH_4 with ^{13}CO (b), which show that the sole products are $^{13}CH_3COOH$ and $CH_3{}^{13}COOH$, respectively.

The activation parameters E_a, A, $\Delta H^{\neq}$, $\Delta S^{\neq}$, and $\Delta G^{\neq}$ at the activated state for the reaction of CH_4 (**3**) and CD_4 (**4**) with CO were calculated by using the Arrhenius and Eyring theories for first-order reaction conditions. The apparent activation energies E_{aH} and E_{aD} and frequency factors A_H and A_D were 16.9 and 19.3 kcal mol^{-1} and 1.7×10^4 and 5.4×10^5 s^{-1}, respectively. These values are reasonable for the abstraction of a hydrogen or deuteron atom from **3** and **4**, respectively, and comparable with those of the oxidation of **3** by $CuCl_2/K_2[PdCl_4]$ mixed catalyst to give methanol.[10] The thermodynamic terms $\Delta H^{\neq}$, $\Delta S^{\neq}$, and $\Delta G^{\neq}$ (253 K) had values of 16.2 and 18.6 kcal mol^{-1}, -40.6 and -34.9 cal mol^{-1} K^{-1}, and 30.5 and 31.0 kcal mol^{-1} for the reactions of **3** and **4**, respectively. In each case, the enthalpy of activation is sufficient for breaking the bond in the transition state. The entropies of activation also covered a significant range and were negative in each case. The lower $\Delta H^{\neq}$ and negative $\Delta S^{\neq}$ values suggest a greater degree of bond forming in the transition state in the case of **3** compared with **4**. From Eyring analysis, the reaction rate constants were $k_H = 9.68 \times 10^{-7}$ and $k_D = 5.63 \times 10^{-7}$ l mol^{-1} s^{-1}, from which the kinetic isotope effect k_H/k_D was calculated to be 1.82 at 80 °C (353 K).

The following evidence allows the possible path of the reaction to be inferred. The use of $^{13}CH_4$ and ^{13}CO resulted in the exclusive formation of $^{13}CH_3COOH$ and $CH_3{}^{13}COOH$, and this reveals that $CH_3^{\bullet}$ is the only methane-derived radical which is trapped by CO[11] to form $CH_3CO^{\bullet}$. The resulting acetyl radical is then converted into **1** via the mixed anhydride with TFA.[4] In the absence of $CaCl_2$, no product was formed. Furthermore, the sufficient $\Delta H^{\neq}$, negative $\Delta S^{\neq}$, and positive isotope effect indicate that the metal species is directly involved in the abstraction of hydrogen from methane to generate methyl radicals, which is the rate-determining step. In addition, in the absence of external CO, not **1** but a small amount of **2** is formed. This result means that CO is also involved in generating the active site of the metal species. The IR spectrum of the solid sample which was prepared from the reaction of $CaCl_2$ and TFA for 4 h shows peaks at 1683.6 ($\tilde{\nu}_{C=O}$) and 1209.1 cm^{-1} ($\tilde{\nu}_{C-O}$), which confirm that $CaCl_2$ is first converted into $Ca(CF_3COO)_2$. Hence, we believe that the active species that abstracts hydrogen from methane is $Ca{-}O^{\bullet}$, which is generated from $Ca(CF_3COO)_2$ by successive reaction with $K_2S_2O_8$ and CO.

We have discovered a new and highly efficient catalyst system that transforms simple alkanes and CO into the corresponding carboxylic acids almost quantitatively. This reaction employs a cheap catalyst, $CaCl_2$, which strongly suggest its use as a substitute for transition metal catalysts and open the door for the use of alkaline earth metals as homogeneous catalysts in C–H activation.

Experimental Section

Representative procedure: The catalyst and $K_2S_2O_8$ were placed in a 25-mL stainless steel autoclave equipped with a Teflon-coated magnetic stirring bar (12 mm, octagonal). Then TFA (5 mL) was added to the autoclave. The autoclave was closed, flushed with methane three times to dislace the air, and pressurized with the desired pressure of methane and CO. The autoclave was then heated with stirring at a fixed temperature for the desired length of time. When the reaction was complete, the autoclave was cooled in an ice bath for 15 min and then opened. About 80 mg of an internal standard (*n*-valeric acid) was added to the reaction mixture, and the content of product was analyzed by gas chromatography (Shimadzu GC-8A). The ester products of methane were analyzed by NMR spectroscopy.

After separating the solution phase from the reaction mixture, the solvent can be separated from acetic acid by distillation (the boiling point difference is sufficient for distillation). The solid spent catalyst and reagents were collected and washed with water to give a clear solution, which is now under investigation.

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BABAR-Phos Rhodium Complexes: Reversible Metal Insertion into a Three-Membered Ring and Catalytic Hydroborations**

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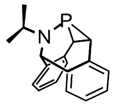
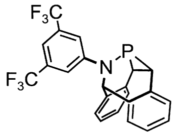
Dedicated to Professor Heinrich Vahrenkamp on the occasion of his 60th birthday

The polycyclic phosphiranes **1a** and **1b** (BABAR-Phos)[1a] are not oxidized by O_2, sulfur, and strongly alkylating agents, and they resist aqueous acids and bases. Furthermore they have electron-withdrawing properties which could make them interesting ligands for hydrosilylation and hydroboration[2] catalysts.[1b] Apart from BABAR-Phos rhodium complexes which were synthesized for this use, we describe here—to our knowledge—the first *reversible* insertion and deinsertion of a metal center into a three-membered heterocycle.[3]

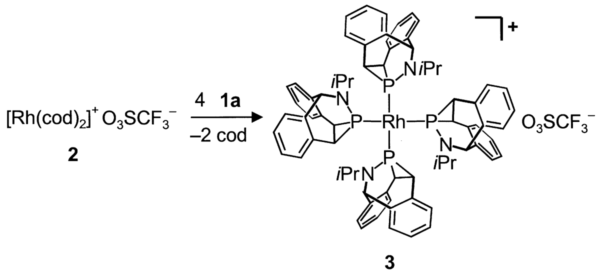
As precursors for the synthesis we used either $[Rh(cod)_2]^+$-$O_3SCF_3^-$ (**2**; cod = 1,5-cyclooctadiene) containing only a weakly coordinating anion or $[Rh_2(\mu_2\text{-}Cl_2)(cod)_2]$ (**4**). Reactions of **2** with **1a** in coordinating solvents, such as acetonitrile, or with the N-aryl-substituted phosphirane **1b** generate brown-red solutions ($\lambda_{max} > 500$ nm), whose ^{31}P NMR spectra display signals in the positive ($\delta = +20$ to $+100$) and negative ($\delta = -60$ to -150) δ range (versus 85 % H_3PO_4). The signals are broadened due to chemical exchange between different species. However, when **2** is treated with **1a** in THF, product **3** is obtained almost quantitatively and independently of the initial ratio **2**:**1a** as poorly soluble, orange microcrystals (Scheme 1). The ^{31}P NMR spectrum of complex **3** shows a doublet at $\delta(^{31}P) = -66.9$ ($^1J(Rh,P) = 170$ Hz), and the complex was structurally characterized by X-ray crystal structure analysis (Figure 1).[4] Remarkably, the Rh center, which is located on a fourfold axis of symmetry, deviates by 0.24 Å from the plane of the square planar arrangement of the four phosphorus atoms (sum of angles at P within the ligand framework: 258°). The Rh–P bond lengths in **3** (2.276(1) Å) are slightly shorter than the ones in other known rhodium phosphirane complexes.[5]



1a
^{iPr}BABAR-Phos



1b
^{BTMP}BABAR-Phos



Scheme 1. Synthesis of complex **3**.

Reactions of the chloride-containing rhodium complex **4** with **1a** or **1b** in weakly coordinating solvents again give brown-red solutions containing several components (exchange-broadened ^{31}P signals in the positive or negative δ range). Only the reaction of **4** with **1b** in acetonitrile leads to one pure product **5** (formula $C_{96}H_{62}Cl_4F_{24}N_6P_4Rh_4$), which is obtained as sparingly soluble, deep brown microcrystals (Scheme 2).

Two of the Cl centers in **5** can be exchanged for poorly coordinating anions X = $O_3SCF_3^-$ or PF_6^- when it reacts with the silver salts **6a** and **6b**, respectively. Deep brown solutions ($\lambda_{max} = 660$ nm) are obtained from which the tetranuclear clusters **7a**, **b** were crystallized. Compound **7b** was also

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