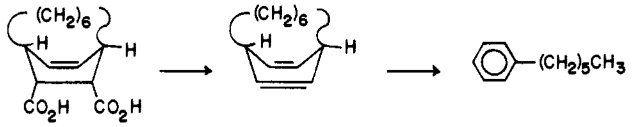
J. Am. Chem. Soc. **1981**, *103*, 217–219

Table II. Atomic Coordinates of All Atoms of **5**

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
O1	0.03852 (7)	0.1997 (2)	0.4133 (1)	H1	0.283 (1)	0.353 (2)	0.322 (2)
O2	0.14304 (8)	−0.0110 (2)	0.4961 (1)	H2A	0.342 (1)	0.070 (2)	0.304 (2)
O3	−0.03582 (7)	0.4425 (2)	0.3388 (1)	H2B	0.349 (1)	0.050 (2)	0.463 (2)
C1	0.27045 (9)	0.2676 (2)	0.3823 (1)	H3A	0.446 (1)	0.308 (2)	0.497 (1)
C2	0.34844 (10)	0.1358 (2)	0.3901 (2)	H3B	0.490 (1)	0.161 (2)	0.405 (2)
C3	0.43765 (10)	0.2412 (3)	0.4069 (2)	H4A	0.423 (1)	0.344 (2)	0.218 (2)
C4	0.44407 (10)	0.3907 (2)	0.3108 (2)	H4B	0.512 (1)	0.417 (2)	0.318 (2)
C5	0.39317 (10)	0.5668 (2)	0.3249 (2)	H5A	0.381 (1)	0.568 (2)	0.412 (2)
C6	0.30576 (11)	0.6027 (2)	0.2299 (2)	H5B	0.436 (1)	0.663 (2)	0.321 (2)
C7	0.22097 (11)	0.6731 (2)	0.2788 (2)	H6A	0.288 (1)	0.499 (2)	0.175 (2)
C8	0.16294 (10)	0.5608 (2)	0.3592 (2)	H6B	0.318 (1)	0.691 (2)	0.173 (1)
C9	0.11791 (9)	0.3912 (2)	0.2935 (1)	H7A	0.175 (1)	0.712 (2)	0.202 (2)
C10	0.17293 (9)	0.2198 (2)	0.3224 (1)	H7B	0.240 (1)	0.782 (2)	0.331 (2)
C11	0.26353 (10)	0.3690 (2)	0.4996 (1)	H8	0.110 (1)	0.641 (2)	0.367 (1)
C12	0.21171 (10)	0.5115 (2)	0.4873 (1)	H9	0.100 (1)	0.411 (2)	0.199 (2)
C13	0.12150 (10)	0.1182 (2)	0.4081 (1)	H10	0.174 (1)	0.151 (2)	0.250 (1)
C14	0.03133 (10)	0.3558 (2)	0.3460 (2)	H11	0.295 (1)	0.324 (2)	0.578 (2)
				H12	0.201 (1)	0.589 (2)	0.548 (2)

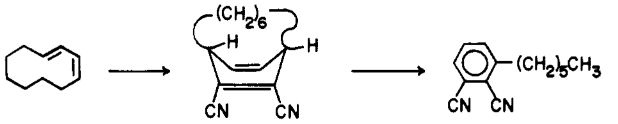
Thermal anisotropic refinement was applied to all nonhydrogen atoms. The positions of all hydrogen atoms were calculated and refined by full-matrix least-squares analysis. The *R* factor for the structure was 0.037. Figure 1 is an ORTEP drawing of **5** with all hydrogens except H-1 omitted for clarity. Table I lists the C–C and C–O bond lengths and the associated bond angles and Table II lists the atomic coordinates of all atoms. As can be seen from Table I, the effect of the internal hydrogen is to significantly distort the six-carbon chain which reaches from one side of the cyclohexene ring to the other. This distortion is reflected both in modified bond angles and slightly elongated C–C bond lengths. Of special interest are the C_1–C_2–C_3 and C_6–C_7–C_8 bond angles which are 107.8° and 123.9°, respectively. In the C_1–C_2–C_3 angle the chain is being sharply turned which results in a reduction of the "normal" C–C–C bond angle. In contrast, the C_6–C_7–C_8 bond angle is being "stretched" around the intruding hydrogen resulting in a significant enlargement of the C–C–C bond angle. Interestingly, the stretching of the six-carbon chain results in the other four C–C–C bond angles in this chain averaging 117.6°.

In order to determine whether these bond distortions would be reflected in thermal stability, we electrochemically bisdecarboxylated **4** in 10% aqueous pyridine with platinum electrodes to obtain 17% of **6**; ^{1}H NMR (C_6D_6) δ 6.23 (2 H, d of d of d, *J* = 1, 3, and 8 Hz), 5.94 (2 H, d of t, *J* = 2 and 8 Hz), 3.17 (1 H, m), 2.91 (1 H, m), 1.79–1.10 (12 H, m); ^{13}C NMR $(CDCl_3)$ δ 138.7 (2 C), 131.6 (2 C), 40.3, 37.0, 32.1, 31.6, 30.9, 29.9, 29.1, 28.3. Heating of a benzene solution of **6** to 165 °C for 8 h resulted in the formation of **7** in 96% isolated yield. The IR and NMR spectra of **7** were identical with those in the literature.[9]



4 **6** **7**

The generality of the thermal conversion of **6** into **7** was confirmed by the addition of dicyanoacetylene to **3** which gave 6% of **8**; mp 68–70 °C; ^{1}H NMR (C_6D_6) δ 5.52 (1 H, d of d of d, *J* = 1, 3, and 7 Hz), 5.25 (1 H, d of d of d, *J* = 1, 6, and 7 Hz), 3.06 (1 H, m), 2.70 (1 H, m), 2.10–0.60 (12 H, m); ^{13}C NMR $(CDCl_3)$ δ 136.4, 135.8, 130.6, 129.9, 115.0, 112.9, 44.6, 39.2, 31.2, 30.5, 30.0, 28.4, 27.8, and 27.3. Heating of **8** to 165 °C for 8 h gave an 81% isolated yield of **9**, which was identified by comparison of its spectra with those of **7**.



3 **8** **9**

In summary, we have prepared the first example of an (i,o)-bicyclo[6.2.2]dodecene derivative and demonstrated that it possessed considerable distortion of its C–C bond properties. We are continuing to explore the chemistry of this system and of other strained derivatives of this general class of compounds.

Acknowledgment. We are indebted to the National Science Foundation for Grant CHE78-10231 which supported this investigation and for Grant CHE77-28505 which aided in the purchase of an Enraf–Nonius X-ray diffractometer. We thank Professors L. Pignolet and J. Gougoutas and Mr. M. McGuiggan for assistance in the X-ray study.

Supplementary Material Available: Tables of bond distances, bond angles, and atom coordinates and an ORTEP drawing of **5** (24 pages). Ordering information is given on any current masthead page.

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(8) All calculations were carried out on a PDP 11/34 computer using the Enraf–Nonius SDP programs. This crystallographic computing package is described by B. A. Frentz, in "Computing in Crystallography", H. Schenck, R. Olthof-Hazekamp, H. van Konigweld, and G. S. Bassie, Eds., Delft University Press, Delft, Holland, 1978, pp 64–71.

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High Methane Formation during the Temperature-Programmed Decomposition in Flowing Hydrogen of Supported Mononuclear and Polynuclear Carbonyl Complexes

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Supported carbonyl complexes are currently receiving wide attention both for their potential applications as an important new class of catalysts and for their utility as models for more traditional types of heterogeneous catalysts.[1-6] Temperature-programmed

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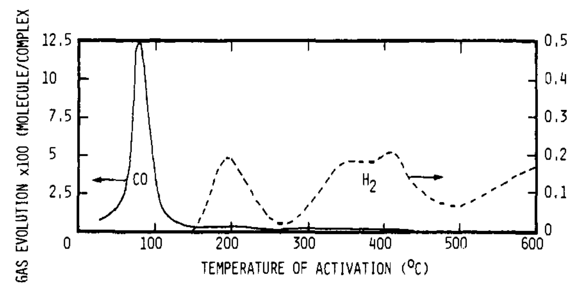

Figure 1. TPDE in flowing He of $Ni(CO)_4/Al_2O_3$. The loading is 0.246% Ni.

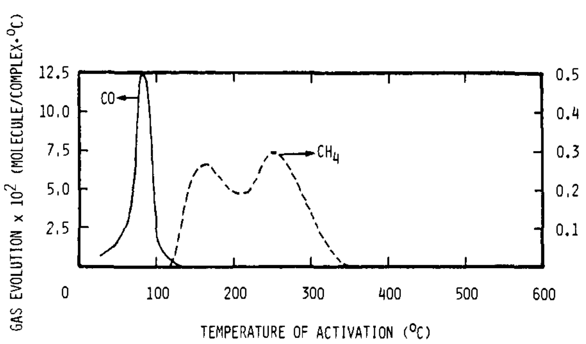

Figure 2. TPDE in flowing H_2 of $Ni(CO)_4/Al_2O_3$. The loading is 0.276% Ni.

decomposition (TPDE), a new experimental technique in which the evolution of gases is monitored during the thermal activation of a catalyst, has proven particularly reliable for revealing the stoichiometric reactions which occur between an adsorbed complex and a support.[7-12] Most studies reported to date have been performed in a sweep gas of He so that fundamental surface processes can be examined. In this paper we report the first detailed study of the TPDE in flowing H_2 of every element which forms a stable carbonyl, demonstrate that these systems have an unexpectedly high propensity to form CH_4, describe the parameters affecting the yield of methane, and compare this stoichiometric reaction to catalytic methanation.

The catalysts were prepared in situ usually by dry mixing and dispersing (at roughly 80 °C) a carbonyl with 0.500 g of 60–80 mesh γ-alumina (Conoco Catapal SB, previously calcined at 500 °C). The $Co_4(CO)_{12}$ and $Rh_6(CO)_{16}$ were obtained from Strem Chemicals, the $V(CO)_6$, $Co_2(CO)_8$, and Fe carbonyls were obtained from Alfa Products, and the remaining carbonyls were obtained from Pressure Chemical. The purities are >98%. The usual use of pentane solvent was minimized to avoid the possibility of some CH_4 being formed by hydrogenolysis. After the mixture was dispersed and cooled to 25 °C, 10 cm^3/min of ultrapure H_2 was flowed through the reactor, and the temperature was raised at 5 °C/min. To obtain the rates of CH_4 and CO evolutions, the effluent was sampled every 6 °C by using an automated Carle gas sampling valve, the gas was separated on a $^1/_8 \times 9$ in. column of Spherocarb (Analabs Inc.) at 25 °C, and the peaks were electronically integrated with a Spectra-Physics System I Computing Integrator. Total evolutions of gases up through C_3 were determined by a back-flush after TPDE as recently described.[9]

The results are tabulated in Table I. By way of example, Figures 1–4 show the TPDE of $Ni(CO)_4/Al_2O_3$ and $Ir_4(CO)_{12}/Al_2O_3$ in sweep gases of He and H_2. (The H_2 observed during TPDE in He is due to a redox reaction between a complex and surface hydroxyl groups.[10]) In addition to CO and CH_4, all catalysts also evolved small amounts of C_2H_4, C_2H_6, and CO_2 during TPDE in H_2 (no C_3 hydrocarbons were detected and no attempt was made to analyze for H_2O). The total amount of C_2 hydrocarbons was about 0.1 molecule/complex (almost all values were in the range 0.05–0.2), and the ratio C_2H_6/C_2H_4 averaged 62 (with most values between 20 and 100). CO_2 evolutions were in the range 0.001–0.008 CO_2/complex, except for $Ni(CO)_4$ which evolved 0.063 CO_2/Ni.

Table I. TPDE in Flowing H_2 of Transition-Metal Carbonyl Complexes Supported on γ-Al_2O_3

complex	loading, % metal	T_{CH_4}, °C[a]	CH_4/ complex	CH_4/ metal atom	C recovery, %
	Mononuclear Complexes				
$V(CO)_6$	0.203	220	0.48	0.48	93
$Cr(CO)_6$	0.207	220	0.43	0.43	97
$Mo(CO)_6$	0.323	190	2.1	2.1	100
$W(CO)_6$	0.483	190	1.91	1.91	98
$Fe(CO)_5$[b]	0.153	170	1.76	1.76	100
$Ni(CO)_4$	0.276	120	0.41	0.41	103
	av for mononuclear complexes:			1.2	
	Dinuclear Complexes				
$Mn_2(CO)_{10}$	0.270	240	0.95	0.48	81
$Re_2(CO)_{10}$	0.556	250	6.52	3.26	101
$Co_2(CO)_8$	0.321	150	2.61	1.31	99
	av for dinuclear complexes:			1.7	
	Cluster Complexes				
$Fe_3(CO)_{12}$	0.332	150	3.29	1.10	89
$Ru_3(CO)_{12}$	0.469	170	8.08	2.69	99
$Os_3(CO)_{12}$	0.777	150	8.49	2.83	94
$Co_4(CO)_{12}$	0.486	150	5.18	1.30	90
$Rh_4(CO)_{12}$	0.391	150	6.09	1.52	83
$Rh_6(CO)_{16}$	0.442	140	7.17	1.20	59
$Ir_4(CO)_{12}$	0.889	140	11.2	2.80	99
	av for cluster complexes:			1.9	

[a] T_{CH_4} is the temperature at which CH_4 is first observed. [b] Impregnation with pentane solvent.

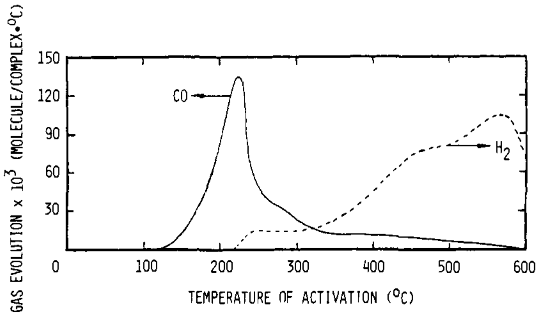

Figure 3. TPDE in flowing He of $Ir_4(CO)_{12}/Al_2O_3$. The loading is 0.907% Ir.

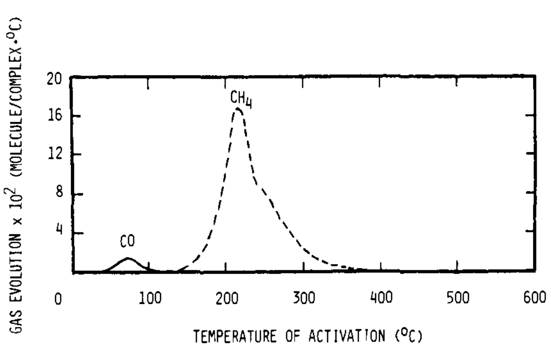

Figure 4. TPDE in flowing H_2 of $Ir_4(CO)_{12}/Al_2O_3$. The loading is 0.889% Ir.

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The yield of higher hydrocarbons is very low. This reflects the fact that in TPDE the primary reaction products are swept from the reactor with very short contact times (~1.4 s).[13] Although the C balance (based on the collection of the above gases) is usually quite good (>90%), in a few cases it is not, most notably for $Rh_6(CO)_{16}$.[15] This could be due to the formation of heavier products (including oxygenates) which are not detected.[16] However, due to the low pressure and short contact times, a more likely explanation may be the formation of some type of Cads (adsorbed carbon) which is unreactive toward H_2.[17]

A notable feature of Table I is the large amounts of CH_4 which are formed, in six cases the conversion of CO to CH_4 exceeding 50%. The yield of CH_4 does not correlate with the activity of the respective metals for catalytic methanation.[18] For example, Ir, the least active of the group 8B metals for methanation, yields far more CH_4 than Ni, one of the most active metals. Examination of Figures 1–4 shows that the thermal stability of a supported complex is the prime factor in determining the quantity of CH_4 formed. Thus $Ni(CO)_4$, which decomposes at a very low temperature (Figure 1), has lost most of its CO before the temperature is high enough to give a reasonable rate of methanation (Figure 2).[19] In contrast, $Ir_4(CO)_{12}$ does not lose its CO until 125 °C (Figure 3).[21] TPDE in flowing H_2 (Figure 4) then yields a curve for CH_4 evolution which is remarkably similar to that for CO evolution in He (Figure 3). Similar correlations are found for the other catalysts.

The two complexes giving the most CH_4 (per complex) are $Ir_4(CO)_{12}$ and $Os_3(CO)_{12}$. These are the same two cluster complexes which were reported to be active for homogeneous catalytic methanation.[22] However, in those experiments the total yield of CH_4 was only about 4 CH_4/complex, whereas several times this amount is now seen to be formed in a purely stoichiometric reaction.[23] Hence, it is possible that the claimed catalytic reaction was in fact stoichiometric (or a heterogeneous reaction[24,25]) and the ability of some cluster complexes (but not mononuclear complexes) to homogeneously yield CH_4 may simply reflect their enhanced thermal stability.

TPDE in flowing H_2 increases the CH_4 yield by 25-fold over TPDE in flowing He.[8] In both He[8] and H_2 (Table I) it is found that the quantity of CH_4 formed is essentially independent of the nuclearity of a complex. This is contrary to some claims that multinuclear sites are necessary to effect the reduction of CO[26] but consistent with more recent work suggesting that mononuclear complexes can be active for methanation.[8,23] Recent data for the TPDE of $Mo(CO)_6/Al_2O_3$ in flowing He and H_2 indicate that sintering of mononuclear precursors to polynuclear sites is probably not a prerequisite for CH_4 formation.[8] (Several experiments in flowing H_2 at loadings between 0.0036 and 0.76% Mo show that the yield of C_2/Mo is independent of loading, again suggesting that multinuclear sites are not involved.) Hydrogenation is not preceded by the disproportionation of CO since the yield of CO_2 is extremely low. Further, in most cases dissociation of CO followed by hydrogenation of Cads is unlikely, since the CH_4 is often formed in a temperature region in which CO is evolved if the TPDE is carried out in flowing He. Hence, it is most likely in these systems that the direct hydrogenation of coordinated CO to CH_4 is occurring at discrete subcarbonyl sites.

In addition to the substantial yields of CH_4 during TPDE in flowing H_2, it is seen (Table I) that the reaction often occurs at temperatures well below that required for catalytic methanation (200–350 °C).[18] An interesting corollary to this result is that a good catalyst for methanation should result if a metal can react with CO to re-form a carbonyl (or subcarbonyl) complex, since a catalytic cycle is now formed. Two of the more active catalysts, Ni and Fe, are in fact the metals which most readily form carbonyls from CO, whereas many of the catalytically less active metals (Ir, Mn, and Cr) do not undergo this reaction.[18,27] However, the most active metal for methanation, Ru, only very slowly forms a carbonyl by exposure to CO under severe conditions, although it was suggested that this may be due to adsorption of $Ru(CO)_5$ which inhibits further reaction.[27] Hydrogenation of carbonyl-like intermediates has been considered as a mechanism for methanation and Fischer–Tropsch synthesis,[28] but currently favored is the dissociation of CO followed by hydrogenation of Cads.[29] Thus, although the facile hydrogenation of coordinated CO is now demonstrated, it is nuclear if this process is important during catalytic methanation. Catalytic methanation over supported carbonyl complexes is currently being studied.

Acknowledgment. Support of this research by the Department of Energy is gratefully acknowledged.

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(13) Hydrocarbon synthesis has been reported for several carbonyl cluster complexes supported on *wet* Al_2O_3 and heated in sealed ampules at approximately 300 °C for ~10^4 s.[14] (H_2 is generated by the water gas shift reaction.)

(14) Smith, A. K.; Theolier, A.; Basset, J. M.; Ugo, R.; Commereuc, D.; Chauvin, Y. *J. Am. Chem.* Soc. **1978**, *100*, 2590.

(15) $Rh_6(CO)_{16}$ also gave a particularly poor C balance for reaction in sealed ampules.[14]

(16) Ichikawa, M. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2273.

(17) TPDE in flowing H_2 of $Mn_2(CO)_{10}$ yielded some CH_4 at temperatures higher than for CO evolution in a sweep gas of He, suggesting some hydrogenation of Cads. However, due to the generally good C balances and the fact that TPDE in H_2 did not significantly improve the C balances compared to TPDE in He, it appears that usually only small quantities of Cads can be formed, and it must be fairly unreactive toward H_2.

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(19) These results are in agreement with less detailed data previously published for $Ni(CO)_4/Al_2O_3$.[20]

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(21) For this experiment the $Ir_4(CO)_{12}$ was dispersed at 125 °C during which time 0.2 CO/complex was evolved.

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(23) The homogeneous reactions were run at 140 °C in toluene solution and gave a turnover frequency of 1×10^{-5} s^{-1}. At 140 °C the extrapolated turnover frequencies for the stoichiometric hydrogenations of $Ir_4(CO)_{12}$ and $Os_3(CO)_{12}$ are also ~1×10^{-5} s^{-1}.

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A Strategy for the Total Synthesis of Jatrophone: Synthesis of Normethyljatrophone

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Received October 1, 1980

Jatrophone (**1**), an architecturally interesting macrocyclic diterpene first isolated in 1970 by the late Professor Kupchan from extracts of *Jatropha gossypiifolia* L. (Euphorbiacae),[1] merits consideration as a synthetic target in that it displays *significant* inhibitory activity against a variety of cell lines, including sarcoma 180, Lewis lung carcinoma, P-388 lymphocytic leukemia, and Walker 256 intramolecular carcinsarcoma.[2] Indeed, extracts of this plant had long been employed in the treatment of cancerous growths.[2]

The structure of jatrophone was based on both chemical and X-ray crystallographic studies.[1] Central to the derived structure

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[†] Camille and Henry Dreyfus Teacher–Scholar, 1978–1983; recipient of a National Institutes of Health (National Cancer Institute) Career Development Award, 1980–1985.

(1) S. M. Kupchan, C. W. Sigel, M. J. Matz, J. A. Saenz Renauld, R. C. Haltiwanger, and R. F. Bryan, *J. Am. Chem. Soc.*, **92**, 4476 (1970); S. M. Kupchan, C. W. Sigel, M. J. Matz, C. J. Gilmore, and R. F. Bryan, *ibid.*, **98**, 2295 (1976).

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