Reaction of Group IV (4[†]) Transition Metal Tetraorganyls with Carbon Monoxide

Karl-Heinz Thiele,* Christian Krüger, and Angela Sorkau

Department of Chemistry, Technical University "Carl Schorlemmer" Merseburg,
DDR-4200 Merseburg, Otto-Nuschke-Str., GDR

Irma Ötvös, Tamás Bartik, and Gyula Pályi*[‡]

Research Group for Petrochemistry of the Hungarian Academy of Sciences,
H-8201 Veszprém, Schönherz Z.u.8., Hungary

Received October 17, 1986

Carbon monoxide reacts with tetrabenzyl, tetrakis(1-naphthylmethyl), and tetra-1-norbornyl compounds of titanium, zirconium, and hafnium. From organic product distribution studies the insertion of CO into one of the metal–alkyl bonds could be identified as the first step. These unstable acyl intermediates are transformed into stable products in different ways. One of the reactions identified is the insertion of the initially formed ketones into the metal–alkyl bond of an unreacted R_4M compound.

Introduction

Reactions of organo transition-metal compounds with carbon monoxide continued to attract great attention in the recent years.[1,2] One of the most interesting currents of this chemistry revealed that dicyclopentadienyltitanium mono- and dialkyls and mono- and diaryls react with CO leading to insertion and subsequent elimination of the acyl groups formed.[3] Zirconocene and hafnocene alkyl or aryl derivatives show a similar chemistry with more stable metal acyl derivatives.[2a,4] The reactivity of the homoleptic R_4M (M = Ti, Zr, Hf) compounds with exclusively σ-bonded organyl groups toward CO is of particular interest in this context. The surprisingly few papers dealing with this problem report the formation of oxygenated, unsatured,[5] and other (unidentified[6]) organic products (with Ti and Zr) as well as very unstable titanium alkyl carbonyl and alkyl acyl derivatives that were characterized by IR spectroscopy.[7] The $Ti(CH_2COOR)_4$ (R = alkyl, aryl) type[8] stable titanium peralkyls showed much reduced reactivity toward CO.[9]

We report here the first results of a study of the reaction of carbon monoxide with R_4M (M = Ti, Zr, Hf; R = benzyl (Bz), 1-naphthylmethyl (Naphme), 1-norbornyl (Nor)) compounds.

Experimental Section

All manipulations involving organometallics were performed by using the standard Schlenk techniques[11] (dried and deoxygenated solvents and Ar and CO gases).

The reaction products were identified by gas chromatography (Hewlett-Packard 5830 A instrument, FID, 20 m × 0.3 mm glass capillary column, coated[12] with OV-1, temperature program was employed, started at 100 °C, heating speed 2 °C/min, to 300 °C; carrier gas Ar, detector FID) and/or mass spectrometry (JEOL-IGO-20K, JEOL-IMS(01) SG-2 instrument). The organic reaction products were identified by comparing the mass spectra with those of authentic compounds and/or literature spectra.[13,14] The quantitative data were obtained from gas chromatography of the benzyl derivatives and from mass spectrometry[15] of the (less volatile) 1-naphthylmethyl and 1-norbornyl compounds.

[†] In this paper the periodic group notation in parenthesis is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13–18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

[‡] Present address: Institute of General and Inorganic Chemistry, L. Eötvös University, H-1088 Budapest, Múzeum krt. 6-8, Hungary.

(1) (a) Calderazzo, F. *Angew. Chem.* **1977**, *89*, 305. (b) Kuhlmann, E. J.; Alexander, J. J. *Coord. Chem. Rev.* **1980**, *33*, 195. (c) Flood, J. C. *Top. Inorg. Organomet. Stereochem.* **1981**, *12*, 37. (d) Blackborrow, J. R.; Daroda, R. J.; Wilkinson, G. *Coord. Chem. Rev.* **1982**, *43*, 17. (e) Herrmann, W. A. *Angew. Chem.* **1982**, *94*, 118. (f) Tkatchenko, I. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 8, Chapter 50.3, pp 101–223. Sneeden, R. P. A. *Ibid.*, Chapter 50.2, pp 19–100. (g) Pályi, G.; Ungváry, F.; Galamb, V.; Markó, L. *Coord. Chem. Rev.* **1984**, *53*, 37. (h) Galamb, V.; Pályi, G. *Corrd. Chem. Rev.* **1984**, *59*, 203. (i) Horwitz, C. P.; Shriver, D. F. *Adv. Organomet. Chem.* 1984, *23*, 219. (j) Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103.

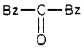
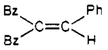
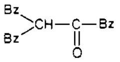
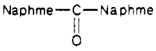
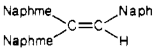
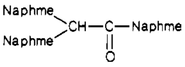
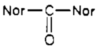
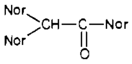
(2) Some recent original papers indicating the main directions: (a) Gell, K. I.; Schwartz, J. *J. Organomet. Chem.* **1978**, *162*, C11. (b) Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 2650. (c) Katahira, D. A.; Moloy, K. G.; Marks, T. J. *Organometallics* **1982**, *1*, 1723. (d) Brinkman, K. C.; Vaughn, G. D.; Gladysz, J. A. *Organometallics* **1982**, *1*, 1056. (e) Bodnar, T. W.; Cutler, A. R. *J. Am. Chem. Soc.* **1983**, *105*, 5926. (f) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1983**, *105*, 1690. (g) Moore, E. J.; Straus, D. A.; Armantrout, J.; Santarsiero, B. D.; Grubbs, R. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2068. (h) Forschner, T. C.; Cutler, A. R. *Organometallics* **1985**, *4*, 1247. (i) Crawford, E. J.; Lambert, C.; Menard, K. P. Cutler, A. R. *J. Am. Chem. Soc.* **1985**, *107*, 3130. (j) Galamb, V.; Pályi, G.; Ungváry, F.; Markó, L.; Boese, R.; Schmid, G. *J. Am. Chem. Soc.* **1986**, *108*, 3344. (k) Tso, C. C.; Cutler, A. R. *Organometallics* **1986**, *5*. (l) Vaughn, G. D.; Gladysz, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 1473. (m) Bianconi, P. A.; Williams, I. D.; Engeler, M. P.; Lippard, S. J. *J. Am. Chem. Soc.* **1986**, *108*, 311. (n) Webb, S. L.; Giandomenico, C. M.; Halpern, J. *J. Am. Chem. Soc.* **1986**, *108*, 345. (o) Tatsumi, K.; Nakamura, A.; Hofmann, P.; Hoffmann, R.; Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 4467. (p) Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1986**, *108*, 6136.

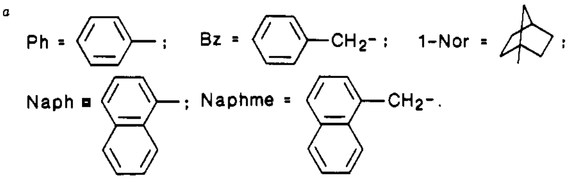
(3) (a) Masai, H.; Sonogashira, K.; Hagihara, N. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 750. (b) Fachinetti, G.; Floriani, C. *J. Chem. Soc., Chem. Commun.* **1972**, *654*, 790. (c) Fachinetti, G.; Floriani, C. *J. Organomet. Chem.* **1974**, *71*, C5. (d) McDermott, J. X.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 947. (e) McDermott, J. X.; Wilson, M. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6529. (f) Demerseman, B.; Bouquet, G.; Bigorgne, M. *J. Organomet. Chem.* **1975**, *93*, 199. (g) de Boer, E. J. M.; ten Cate, L. C.; Staring, A. G. I.; Teuben, J. H. *J. Organomet. Chem.* **1978**, *181*, 61. (h) Dormond, A.; Dahchour, A. *J. Organomet. Chem.* **1980**, *193*, 321. (i) Teuben, J. H.; de Boer, E. J. M.; Klazinga, A. H.; Klei, E. *J. Mol. Catal.* **1981**, *13*, 107.

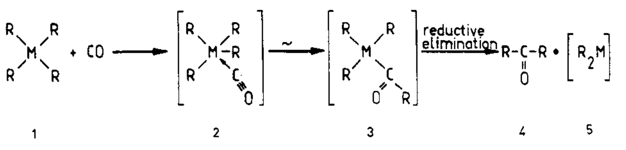
(4) (a) Bertelo, C. A.; Schwartz, J. *J. Am. Chem. Soc.* **1975**, *97*, 228. (b) Fachinetti, G.; Floriani, C.; Marchetti, F.; Merlino, S. *J. Chem. Soc., Chem. Commun.* **1976**, 522. (c) Fachinetti, G.; Fochi, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1977**, 1946. (d) Erker, G.; Rosenfeldt, F. *Angew. Chem.* **1978**, *90*, 640. (e) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716. (f) Lappert, M. F.; Luong-Thi, N. T.; Milne, C. R. C. *J. Organomet. Chem.* **1979**, *174*, C35. (g) Erker, G.; Rosenfeldt, F. *J. Organomet. Chem.* **1980**, *188*, C1. (h) Erker, G.; Kropp, K. *J. Organomet. Chem.* **1980**, 194, 45. (i) Baldwin, J. C.; Keder, N. L.; Strouse, C. E.; Kaska, W. C. *Z. Naturforsh. B: Anorg. Chem., Org. Chem.* **1980**, *35B*, 1289. (j) Wolczanski, P. T.; J. E. *Acc. Chem. Res.* **1980**, *13*, 121. (k) Jeffrey, J.; Lappert, M. F.; Luong-Thi, N. T.; Webb, M.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* 1981, 1593. (l) Bristow, G. S.; Lappert, M. F.; Martin, T. R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.*

0276-7333/87/2306-2290$01.50/0

Table I. Products of R_4M/CO Reactions (M = Ti, Zr, Hf)[a]

R_4M	primary product	subsequent products
Bz_4Ti	 $Bz{-}C({=}O){-}Bz$	 $Bz_2C{=}C(Ph)H$
Bz_4Hf		 $Bz_2CH{-}C({=}O){-}Bz$ Bz-CHOH-Bz Bz-Bz, BzH
$(Naphme)_4Ti$	 $Naphme{-}C({=}O){-}Naphme$	 $Naphme_2C{=}C(Naph)H$
$(Naphme)_4Zr$		 $Naphme_2CH{-}C({=}O){-}Naphme$ Naphme-CHOH-Naphme Naphme-Naphme, NaphmeH
$(1\text{-}Nor)_4Ti$	no reaction	
$(1\text{-}Nor)_4Zr$	 $Nor{-}C({=}O){-}Nor$	 $Nor_2CH{-}C({=}O){-}Nor$ Nor-CHOH-Nor Nor-Nor, NorH

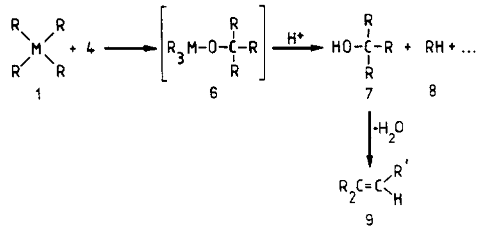
[a] 



Scheme I

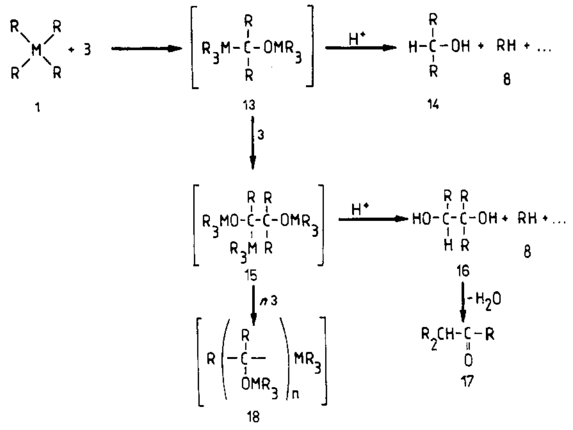
M: Ti, Hf; R: Bz, Naphme
Zr R: Naphme, Nor

Scheme II



M: Ti, Hf; R: Bz, Naphme; R': Ph, Naph
Zr R: Naphme; R': Naph

Scheme III



M: Ti, Hf; R: Bz, Naphme; M: Zr; R: Naphme, Nor

The group IV (4) peralkyls (1), used as starting materials, were prepared by published procedures: Bz_4Ti[16] (**1a**), Bz_4Hf[17] (**1b**), $(1\text{-}Naphme)_4M$ (M = Ti (**1c**), Zr (**1d**), Hf (**1e**),[18] $(1\text{-}Nor)_4Ti$[19] (**1f**), and $(1\text{-}Nor)_4Zr$[20] (**1g**). Other materials were of commercial origin or prepared by standard procedures.

Reaction of R_4M Compounds with Carbon Monoxide. The R_4M compound (1.1 mmol) was dissolved in 30 mL of toluene under Ar. Then the solution was transferred into a thermostated reaction vessel equipped with a magnetic (external) stirrer and a gas burette. The atmosphere was changed to CO and the solution was stirred for 40 h at 25 °C. Subsequently the reaction mixture was cooled to −40 °C, and 5–10 mL of dry, cold methanol was added (protolysis)[2a,5a,21] still under exclusion of air. (The Ti-containing reaction mixtures were brown and discolored upon protolysis. The others were colorless already before addition of the methanol.) Then the reaction mixture was left to warm to room temperature, the solvents were evaporated at reduced pressure, and the solid residue was analyzed as described above. The mass spectral data are tabulated in Table III (supplementary material).

---

(5) (a) Attridge, C. J.; Dobbs, B.; Maddock, S. *J. Organomet. Chem.* **1973**, *57*, 255. (b) Demin, E. A.; Tshalganov, E. M.; Kurtshenko, E. H. *Zh. Obshch. Khim.* **1976**, *46*, 2561.

(6) Calderazzo, F. *Pure Appl. Chem.* **1973**, *33*, 453.

(7) Röder, A.; Thiele, K.-H.; Pályi, G.; Markó, L. *J. Organomet. Chem.* **1980**, *193*, C31.

(8) Sorkau, A.; Thiele, K.-H.; Galamb, V.; Pályi, G. *Z. Allg. Anorg. Chem.* **1986**, *532*, 47.

(9) The comparison of the reactivity of early- (Ti, Zr, Hf) and late- (Co) transition-metal alkyl derivatives toward CO is one of the main goals of the cooperation between our laboratories. Compare ref 1h, 2j, 7, 8, and 10.

(10) (a) Nagy-Magos, Z.; Bor, G.; Markó, L. *J. Organomet. Chem.* **1968**, *14*, 205. (b) Pályi, G.; Galamb, V.; Röder, A. *Atti Accad. Sci. Bologna, Cl. Sci. Fis.* **1981**, *269*(13/8), 67. (c) Galamb, V.; Pályi, G.; Cser, F.; Furmanova, M. G.; Struchkov, Yu. T. *J. Organomet. Chem.* **1981**, *209*, 183. (d) Galamb, V.; Pályi, G.; *J. Chem. Soc., Chem. Commun.* **1982**, 487.

(11) (a) Herzog, S.; Dehnert, J. *Z. Chem.* **1964**, *4*, 1. (b) Shriver, D. F. "*Manipulation of Air-Sensitive Compounds*"; McGraw-Hill: New York; **1969**.

(12) (a) Simon, Á.; Ötvös, I.; Pályi, G. *Kém. Közl.* **1972**, *37*, 81. (b) Alexander, G.; Garzó, G.; Pályi, G. *J. Chromatogr.* **1974**, *91*, 25.

(13) (a) *Eight Peak Index of Mass Spectra*; Publishing Mass Spectrometry Data Centre, AWRE: Reading, Aldermaston, 1970; Vols. I, Ii. (b) *Atlas of Mass Spectral Data*; Stenhagen, E., Abrahamsson, S., McLafferty, F. W.; Eds., Interscience: New York, 1969; Vols. 1–3.

(14) Leading references. Benzyl derivatives: (a) Grubb, H. M.; Meyerson, S. In *Mass Spectrometry of Organic Ions*; McLafferty, F. W., Ed.; Academic: New York, 1963; pp 453–527. (b) Smith, D. H. *Anal. Chem.* **1972**, *44*, 536. (c) Gillis, R. G. *Org. Mass Spectrom.* **1971**, *5*, 79. Naphthylmethyl compounds: (d) Alpin, R. T.; Safe, S. *Chem. Commun.* **1967**, 140. (e) Schwarz, H.; Bohlmann, F. *Org. Mass Spectrom.* **1973**, *7*, 23. Norbornyl compounds: (f) Goto, F.; Tetematsu, A.; Hata, Y.; Muneyuki, R.; Tanida, H.; Tori, R. *Tetrahedron* **1966**, *22*, 2213. (g) Meyerson, S.; Weitkamp, A. W. *Org. Mass. Spectrom.* **1968**, *1*, 659. (h) Golovkina, L. S.; Rusinova, G. V.; Sokolova, I. M.; Matveeva, I. A.; Gervits, A. S. *Org. Mass Spectrom.* **1979**, *14*, 629. (i) Matveeva, I. A.; Sokolova, I. M.; Golovkina, L. S.; Belikova, N. A.; Rusinova, G. V.; Kovalenko, L. I., *Izv. Akad. Nauk SSSR, Ser. Khim.* **1981**, *2*, 319.

(15) See, for example: Beynon, J. H. *Mass Spectrometry and its Applications to Organic Chemistry*; Elsevier: Amsterdam, 1960; pp 424–432.

(16) Zdunneck, P.; Thiele, K.-H. *J. Organomet. Chem.* **1970**, *22*, 659.

(17) Felten, J. J.; Andersen, W. P. *J. Organomet. Chem.* **1972**, *36*, 87.

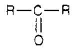
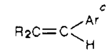
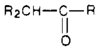
(18) Scholz, J.; Thiele, K.-H. *Z. Anorg. Allg. Chem.* **1986**, *541*, 116.

(19) Bower, B. K.; Tennent, H. G. *J. Am. Chem. Soc.* **1972**, *94*, 2512.

(20) Dimitrov, V.; Thiele, K.-H.; Schenke, D. *Z. Anorg. Allg. Chem.* **1985**, *527*, 85.

(21) (a) Zucchini, U.; Giannini, U.; Albizzati, E.; D'Angelo, R. *J. Chem. Soc., Chem. Commun.* **1969**, 1174. (b) Zucchini, U.; Albizzati, E.; Giannini, U. *J. Organomet. Chem.* **1971**, *26*, 357. (c) Bower, B. K.; Tennent, H. G. *J. Am. Chem. Soc.* **1972**, *94*, 2512. (d) Collier, M. R.; Lappert, M. F.; Pearce, R. *J. Chem. Soc., Dalton Trans.* **1973**, 445. (e) Lappert, M. F.; Patil, D. S.; Pedley, J. B. *J. Chem. Soc., Chem. Commun.* **1975**, 830. (f) Basso-Bert, M.; Gervais, D. *J. Organomet. Chem.* **1979**, *165*, 209.

Table II. Distribution of the Main Reaction Products of R_4M + CO

		products[a,b] %			
M	R	 $R-\overset{\displaystyle O}{\overset{\|}{C}}-R$	 $R_2C{=}C(Ar)H$[c]	 $R_2CH-\overset{\displaystyle O}{\overset{\|}{C}}-R$	$R_2CH(OH)$
Ti	$PhCH_2$[d,e]	8–11	61–83	6–19	4–12
Hf	$PhCH_2$[e]	3	76	12	3
Ti	Naphme[f]	48	30	10	12
Zr	Naphme[f]	53	13	7	27
Hf	Naphme[f]	42	21	8	29
Zr	Nor[e]	50		27	23

[a] Relative product ratios. [b] R–R and RH represented always 1–2%. [c] Ar = Ph or Naph. [d] Values from different runs. [e] Data from GLC and MS measurements. [f] Data only from quantitative MS, reliable to 10–15 relative mol %.[15]

During the protolysis a weak gas evolution was observed. This gas was analyzed for the Bz_4Ti reaction. The GC analysis (Carlo Erba ATC/f instrument, 2 m × 4 mm (i.d.) glass column, Porapack Q (80/120 mesh) stationary phase, 25 °C, carrier gas 10 mL/min Ar, detector TC) of the reaction mixture revealed that the gas evolved was H_2, approximately corresponding to 25 mol % of the starting Ti.

Reaction of Tetrabenzyltitanium with Benzophenone. Tetrabenzyltitanium, $(PhCH_2)_4Ti$ (494 mg, 1.2 mmol), was dissolved in 40 mL of toluene in a thermostated reaction vessel with external magnetic stirrer under Ar atmosphere. The solution was cooled to −78 °C, and while the solution was stirred, benzophenone, Ph_2CO (473 mg, 2.6 mmol), was added in 3–5 portions during 1 h. After the benzophenone has been added, the cold solution was stirred for 20–30 min and then left to warm to room temperature and stirred for further 24 h. An orange precipitate was formed that was isolated by filtration, washed with cold toluene, and dried under vacuum at room temperature. This precipitate was then treated with 10 mL of methanol and analyzed as described before. The product was identified as triphenylethylene by MS (cf. Table III).

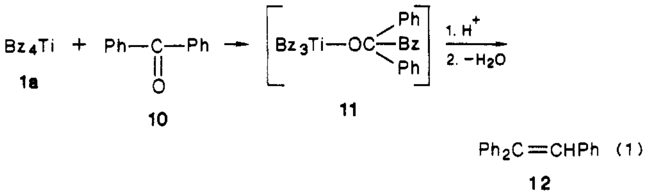
Results and Discussion

The toluene solutions of the group IVB (4) tetraorganyls **1a–g** readily absorb carbon monoxide at room temperature under 1 bar of pressure. The CO absorption is accompanied by the change of the color from deep red to brown (for Ti alkyls) and the formation of a black precipitate. After the reaction has been finished (CO absorption stops), the reaction mixture was treated with methanol to achieve the protolytic cleavage of metal-containing products.[2a,5a,21] In solutions obtained in this way, ketones, secondary alcohols, alkenes, and hydrocarbons of the RH and R–R type were detected. A survey of the organic products found in the reaction mixtures is given in Table I. Mixtures of similar organic products were found to be formed upon carbonylation of alkyl- and aryllithium compounds.[22] The distribution of the products is given in Table II. The formation of the organic products listed in Tables I and II can be rationalized as shown in Schemes I–III.

The sequence of the primary reactions is shown in Scheme I. Formation of the monocarbonyl intermediate **2** can be supposed to proceed as the primary step.[1j,2a,3c,4d,e,g,7] The rapid insertion of the coordinated carbonyl into one of the M–C bonds is based on well-documented analogies.[1j,2a,3c,4a–d,g,5a] The alkyl–acyl derivatives **3** formed in this manner should be very reactive,[1j,3c,b,7] and evidently the most favored reaction path is the reductive elimination[3b,c,23] of ketones **4** and formation of the low-valent species **5**. Compound **4** derivatives were found analytically, **5a** was detected by evolution of hydrogen in the protolysis with methanol.[24] (An intermolecular pathway providing the same ketone but a Ti(III) species as an organometallic product cannot be ruled out either.)

Obviously, the reactive **1** and **3** readily react with most major components of the reaction mixture. From the possible combinations, those involving **1** + **4** and **1** + **3** could be indentified through the organic products, by a kind of retrosynthetic analysis (Schemes II and III).

The reaction of group IV (4) metal organics with aldehydes or ketones is of very important synthetic potentiality. However, only a few reports[25] have appeared as yet. We performed a model experiment to explore this reaction possibility. In fact we found that **1a** reacts with benzophenone (**10**) according to reaction sequence (1) giving triphenylethylene (**12**) as the only organic product. Intermediate **11** is supposed on the basis of well-documented[25d,e] analogies, the easy dehydration of the tertiary carbinol from the alkoxy ligand of **11** is trivial,[26] and **12** could be isolated and identified.



The metal-bound carbonyl group of the alkyl–acyl intermediates **3** can be assumed to react similarly with **1** as that of ketones **4** (or **10**) (Scheme III). In this reaction the dinuclear alkyl–alkoxide bridged intermediate **13** can give secondary alcohols **14** (which could be detected within the products) or, through the reaction with a further molecule of **3**, the instable diols **16** that should readily be dehydrated to ketones **17** which were found, in fact, in the reaction

---

(22) Leading references: (a) Wittig, G. *Angew. Chem.* **1940**, *53*, 241. (b) Jutzi, P.; Schröder, F.-W. *J. Organomet. Chem.* **1970**, *24*, 1. (c) Trzupek, L. S.; Newirth, T. L.; Kelly, E. G.; Sbarbati, N. E.; Whitesides, G. M.; *J. Am. Chem. Soc.* **1973**, *95*, 8118. (d) Nudelman, N. S.; Vitale, A. A. *Org. Prep. Proced. Int.* **1981**, *13*, 144. (e) Seyferth, D.; Weinstein, R. M. *J. Am. Chem. Soc.* **1982**, *104*, 5534. (f) Seyferth, D.; Weinstein, R. M., Wang, W.-L. *J. Org. Chem.* **1983**, *48*, 1144. (g) Nudelman, N. S.; Vitale, A. A. *J. Organomet. Chem.* **1983**, *241*, 143. (h) Seyferth, D.; Weinstein, R. M.; Wang, W.-L.; Hui, R. C. *Tetrahedron Lett.* **1983**, *24*, 4907. (i) Narayana, C.; Periasaning, M. *Synthesis* **1985**, 253 and references cited therein.

(23) (a) Murray, J. G. *J. Am. Chem. Soc.* **1961**, *83*, 1287. (b) Demerseman, B.; Bauquet, G.; Bigorgne, M. *J. Organomet. Chem.* **1975**, *93*, 199.

(24) (a) Martin, H.; Stedefelder, J. *Liebigs Ann. Chem.* **1958** *618*, 17. (b) Thiele, K.-H.; Röder, A.; Mörke, W. *Z. Anorg. Allg. Chem.* **1978**, *441*, 13.

(25) Ti: (a) Ballard, D. G. H.; Janes, W. H.; Medinger, T. *J. Chem. Soc. B* **1968**, 1168. (b) Coutts, R. S. P.; Wailer, P. C.; Martin, R. L. *J. Organomet. Chem.* **1973**, *50*, 145. (c) Huffman, J. C.; Moloy, K. G.; Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 3009. (d) Reetz, M. T.; Steinbuch, R.; Westermann, J.; Peter, R. *Angew. Chem.* **1980**, *92*, *1044*. (e) Blandy, C.; Gervais, G. *Inorg. Chim. Acta* **1981**, *52*, 79. (f) Gamgarotta, S.; Floriani, C.; Chiese-Villa, A.; Guostini, C. *Organometallics* **1986**, *5*, 2425. Zr: (g) Razuvajev, G. A.; Vyshinskaya, L. I.; Aviasileva, G.; Malisheva, A. V.; Mar'in, V. P. *Inorg. Chim. Acta* **1980**, *44*, L285.

(26) See, for example: Asinger, F.; Berger, W.; Fanghaenel, E.; Müller, K. R. *J. Prakt. Chem.* **1963**, *22*, 153.

mixture. The oligomeric product 18 is most probably the insoluble residue of the reaction mixture; its further characterization is in progress. The formation of 18 would be of a certain importance since it is likely a functionalized CO oligomer derivative.

The formation of hydrocarbons RH (8) and R–R after the protolysis of the reaction mixtures results from the presence of unchanged R–M bonds. It should be noted that (at least formally) reductive elimination of the R–R species in the protolytic cleavage of tetrabenzyl–transition-metal derivatives has been reported by one of us.[27]

There is a distinct difference in the behavior of tetra-1-norbornyl derivatives **1f** and **1g** with respect to arylmethyl compounds **1a–e**. In the case of **1f** no reaction with CO has been observed within several days. This finding is in agreement with the observation[20] that other polar molecules, such as hydrogen halides or alcohols, react with the sterically shielded titanium atom in **1f** only very slowly or not at all. By contrast, the sterically less hindered Zr derivative **1g** reacts readily with CO and the product of the primary reaction (ketone **4g**) could be detected. The dinorbornyl ketone seems, however, to be too bulky to attack **1g** while, however, reaction products (Scheme III) of the alkyl–acyl intermediate **3g** with **1g** (i.e. alcohol 14 and ketone 17) could be detected.

It can be concluded that tetraorganyls of Ti, Zr, and Hf react readily with CO if the metal is not too shielded sterically. The primary reactions lead to the formation of symmetrical ketones. Subsequent reactions of these ketones and acyl metal type intermediates with the starting tetraorganyls provide secondary alcohols, asymmetric ketones, and trisubstituted ethylene derivatives. The reactions deduced from distribution of the organic products resemble more the reactivity of main-group organometallics (especially Li[22]) than that of late-transition-metal organyls.[1,25f,28] This difference should be attributed mostly to (i) the high number of alkyl groups in the R_4M compounds, (ii) the oxophilic nature[2c,f,3c,4b,e,j,25f] of the group IVB (4) transition metals, and (iii) the well-documented possibility of the formation of M–O–C–M moieties in the CO-derived chemistry of these metals.[2a,b,4j,30]

Acknowledgment. We thank Dr. J. Scholz and Dipl. Chem. D. Schenke (Merseburg, GDR) for help in the preparation of the starting materials and to Mrs. E. Fekete (Veszprêm, Hungary) for assistance in performing the analyses.

Registry No. 1a, 17520-19-3; 1b, 31406-67-4; 1c, 34074-41-4; 1d, 34074-40-3; 1e, 108815-98-1; 1f, 110241-91-3; 1g, 110241-90-2; 4 (R = $PhCH_2$), 102-04-5; 4 (R = NaphMe), 51042-38-7; 4 (R = Nor), 110223-83-1; 9 (R = $PhCH_2$, Ar = Ph), 50485-27-3; 9 (R = NaphMe, Ar = Naph), 110223-84-2; 10, 119-61-9; 12, 58-72-0; 14 (R = $PhCH_2$), 5381-92-0; 14 (R = NaphMe), 110223-87-5; 14 (R = Nor), 110223-88-6; 17 (R = $PhCH_2$), 50485-28-4; 17 (R = NaphMe), 110223-85-3; 17 (R = Nor), 110223-86-4; CO, 630-08-0.

Supplementary Material Available: Table III, mass spectral data of the organic products (3 pages). Ordering information is given on any current masthead page.

---

(27) Thiele, K.-H.; Köhler, E.; Adler, B. *J. Organomet. Chem.* **1973**, *50*, 153.

(28) Representative examples of the "oxophobic" nature of the late transition metals: (a) Volpin, M. E.; Kolominkov, I. S. *Organomet. React.* **1975**, *5*, 313. (b) Bianco, V. D.; Doronzo, S.; Gallo, N. *Inorg. Nucl. Chem. Lett.* **1981**, *17*, 75. (c) Johnson, D. L.; Gladysz, J. A. *Inorg. Chem.* **1981**, *20*, 2508. (d) Walther, D.; Dinjus, E.; Sieler, J. *Z. Chem.* **1983**, *23*, 237. (e) Darensbourg, D. J.; Kudaroski, R. A. *Adv. Organomet. Chem.* **1983**, *22*, 129. (f) Tasi, M.; Pályi, G. *Organometallics* **1985**, *4*, 1523.

(29) Further leading papers documenting the "oxophilic" nature of the early transition metals: (a) Fischer, E. O.; Fontana, S. *J. Organomet. Chem.* **1972**, *40*, 159. (b) Schmid, G.; Bätzel, V.; Stutte, B. *J. Organomet. Chem.* **1976**, *113*, 67. (c) Stutte, B.; Bätzel, V.; Boese, R.; Schmid, G. *Chem. Ber.* **1978**, *111*, 1603. (d) Schmid, G.; Stutte, B.; Boese, R. *Chem. Ber.* **1978**, *90*, 417. (f) Berry, D. H.; Bercaw, J. E.; Jircitano, A. J.; Mertes, K. B. *J. Am. Chem. Soc.* **1982**, *104*, 4712. (g) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1983**, *105*, 1690. (h) Barger, P. T.; Bercaw, J. E. *Organometallics* **1984**, *3*, 278.

(30) (a) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 6733. (b) Fachinetti, G.; Floriani, C.; Roselli, A.; Pucci, S. *J. Chem. Soc., Chem. Commun.* **1978**, 269. (c) Gell, K. I.; Williams, G. M.; Schwartz, J. *J. Chem. Soc., Chem. Commun.* **1980** 550. (d) Erker, G.; Kropp, K. *Chem. Ber.* **1982**, *115*, 2437. (e) Erker, G.; Kropp, K; Krüger, C.; Chiang, A.-P. *Chem. Ber.* **1982**, *115*, 2447.

Activation of C–H Bonds of Aromatic Rings Using Calcium Atoms[1]

Kunio Mochida,* Yoo Hiraga, Hidenori Takeuchi, and Hiroyasu Ogawa

Department of Chemistry, Faculty of Sciences, Gakushuin University, 1-5-1 Mejiro, Tokyo 171, Japan

Received October 22, 1986

Calcium atoms inserted into C–H bonds of aromatic rings in benzene, alkylbenzenes, phenyltrimethylsilane, and xylenes to give the corresponding arylcalcium hydrides. Arylcalcium hydrides reacted with trimethylchlorosilane to give aryltrimethylsilanes and the reduced product (trimethylsilane). Trimethylsilyl-substituted positions on aromatic rings of the aromatic compounds reflected the spin densities on the aromatic rings in the aromatic compound anion radicals. The aromatic compound anion radicals generated by the reactions of calcium atoms with aromatic compound vapors were also detected by ESR. Arylcalcium hydrides reacted with various organic substances to give aryl-substituted substrates and reduced substrates.

Introduction

The study of a metal–vapor reaction has been of considerable interest in organometallic chemistry and organic synthesis during the last few decades.[2] With these methods, it is proving feasible to synthesize organometallic compounds which would be difficult, if not impossible, to

---

(1) Preliminary results of this study see: Mochida, K.; Takeuchi, H.; Hiraga, Y.; Ogawa, H. *Chem. Lett.* **1984**, 1989.

(2) For example: (a) Blackborow, J. R. *Metal Vapor Synthesis in Organometallic Chemistry*; Springer-Verlag: New York, 1979. Klabunde, K. J. *Chemistry of Free Atoms and Particles*; Academic: New York, 1980. Klabunde, K. J. *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum: New York, 1980, Chapter 2.

0276-7333/87/2306-2293$01.50/0