additional evidence that the cyclopropane rings are intact in **3a** or **3b**.

Irradiation of **3a** or **3b** in protonated solvents also results in the formation of **5**. In deuterated solvents (C_7D_8, C_6D_6, or C_6D_{12}) photolysis results in the formation of the deuteride hydride, $IrClHD[P(H_2C(C_3H_5))(CMe_3)_2]_2$, perhaps by homolysis of the Ir–C bond with consequent formation of radicals that pick up deuterium from the solvent.

We are currently investigating the reactions of other cyclopropyl phosphines with group 8 metals and the further reactions of the five-coordinate, 16-electron iridium(III) compounds reported here.

Acknowledgment. This work was kindly supported by the National Science Foundation (CHE80-09671).

Registry No. 1, 84081-80-1; **2**, 84081-81-2; **3a**, 84129-17-9; **3b**, 84081-82-3; **4**, 84081-83-4; **5**, 84081-84-5; $[IrCl(C_8H_{14})_2]_2$, 12246-51-4; $IrClHD[P(H_2C(C_3H_5))(CMe_3)_2]_2$, 84081-85-6.

Synthesis of Carbene Complexes of Group 4 Metals from Alkylidene-Bridged Heterobimetallic Precursors

Frederick W. Hartner, Jr., Jeffrey Schwartz,* and
Susan M. Clift

Department of Chemistry, Princeton University
Princeton, New Jersey 08544

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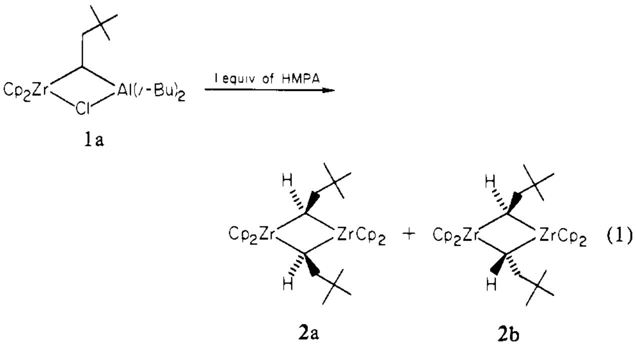
In contrast to carbene complexes of groups 5[1] and 6[2] metals, which have been extensively studied, knowledge of carbene complexes of group 4 metals is limited to one observed Zr species[3] and several postulated Ti intermediates.[4,5] This relative lack of information may be due to limitations in synthetic techniques heretofore available and not to any inherent instability of members of this class.

When zirconium complex **1a**[6] is treated with 1 equiv of hexamethylphosphoramide (**warning**: cancer suspect; a good ligand for aluminum complexes[7]), red-brown crystals can be isolated (31% yield) whose ^1H NMR spectrum[8] suggests it to be a mixture of carbene dimerization products **2a** and **2b** (3:1).[9] We reasoned that if a bridged alkylidene complex were treated with HMPA *in the presence of another ligand that would strongly coordinate the transition-metal carbene complex* thus formed, the latter species might possess sufficient stability to enable its direct observation and examination in subsequent reactions. Thus, when a solution of, for example, **1a** and triphenylphosphine (which should be a good ligand for Zr(II)[10]) is treated with 1 equiv of HMPA (toluene, −40 °C) and is allowed to warm to room temperature over a period of 15 min, a mixture is obtained whose ^1H HMR spectrum is consistent with the formation of carbene complex **3a**, which could be purified[11] as a yellow-orange oil by concentrating the toluene solution, adding pentane, cooling to −78 °C, removing the pentane supernatant from the precipitate formed, and evaporating the solvent. Proton NMR analysis of the pentane-soluble oil showed it to be **3a**[12] and the precipitate to be **4**. A similar procedure gives $Cp_2Ti(CH_2)(PEt_3)$, **5** (Cp = cyclopentadienyl). For **1a**, small amounts of three other Cp-containing products are noted.[13] Two of these are the dimers **2a** and **2b**. The third becomes the major Cp-containing product when a reaction, similar to the one described above, is carried out with 2 equiv of HMPA and no other organophosphine. On the basis of ^1H and ^{31}P NMR studies, its structure is assigned to be **3a″**.



3:1 yield

Low-temperature ^1H and ^{31}P NMR analysis shows that HMPA forms a complex with **1a** on mixing at −30 °C. Signals for carbene complex **3a** appear in the presence of PPh_3 slowly at −10 °C; at +10 °C the reaction is complete within 1 h. The titanium system is more reactive; activation of **2** by HMPA in the presence of triethylphosphine gives the corresponding titanium complex (**5**) on mixing at −30 °C.

Yields vary for formation of carbene complexes **3** as a function of trapping phosphine ligand used (see Table III).[14] In general, strong σ-donor phosphines of small cone angle[15] are favored for complexation relative to HMPA and for increasing thermal stability of the carbene species. For **3a′** the half-life for decomposition (at room temperature in solution) is ca. 1 week, for **3a** several days, and for the HMPA complex **3a″** several hours.

As the alkylidene unit of **1** becomes sterically *less* crowded, *lower* yields of carbene complexes are obtained by reaction with HMPA and a phosphine. Cyclohexanone treatment of the reaction mixtures obtained from **1e** gives, on hydrolysis, a significant amount of cyclohexanol (37% based on **1e**), and analysis of the reaction mixture prior to hydrolysis also showed the presence of a neohexenylzirconium species. These facts infer that β-H elimination occurs to give an aluminum hydride (in reversal of the synthesis procedure for **1**);[5] this process may compete with carbene complex formation. In this way, reaction partitioning might depend on substitution at the γ position of the alkyl chain, reflecting the ease of attainment of a preferred dihedral angular relationship between a β C–H bond and the α Al–C bond:[16] bulky

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(5) Ott, K. D.; Grubbs, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 5922.

(6) Hartner, F. W., Jr.; Schwartz, J. *J. Am. Chem. Soc.* **1981**, *103*, 4979.

(7) Mole, T.; Jeffrey, E. A. "Organoaluminum Compounds"; Elsevier: New York, 1972; p 110.

(8) NMR spectra were recorded in toluene-d_8. ^{31}P NMR shifts are referenced to external H_3PO_4 (positive to low field).

(9) Hydrolysis of the **2a**–**2b** mixture gave cyclopentadiene and 3,3-dimethylbutane as the sole organic products.

(10) Gell, K. I.; Schwartz, J. *J. Am. Chem. Soc.* **1981**, *103*, 2687.

(11) We thank Professor R. H. Grubbs for suggesting this type of purification scheme.

(12) H–P coupling constant data are inconsistent with an ylide structure (see ref 3).

(13) These were carried through the purification procedure in small amount with the carbene complex.

(14) Yields for the formation of other neohexylidene zirconocene complexes include $PMePh_2$ (63%), $P(p\text{-}C_6H_4OMe)_3$ (64%), and $P(p\text{-}C_6H_4F)_3$ (37%).

(15) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

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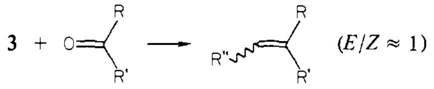
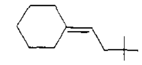
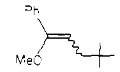
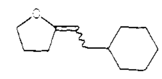
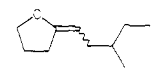
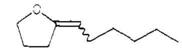
Table I. NMR Spectroscopic Data (δ) for Selected Complexes[a,b]

complex	H_α	H_β	C_5H_5	$C(CH_3)_3$	$^{13}C_\alpha$	^{31}P
2a	9.07 (1 H, t, J = 7.0 Hz)	1.88 (2 H, d, J = 7.0 Hz)	6.06 (5 H, s) 6.02 (5 H, s)	0.53 (9 H, s)		
2b	8.63 (1 H, t, J = 6.7 Hz)	2.34 (2 H, d, J = 6.7 Hz)	6.09 (10 H, s)	0.46 (9 H, s)		
3a	11.71 (1 H, ddd, J = 12.0, 5.5, 4.1 Hz)	3.66 (1 H, ddd, J = 12.0, 15.7, 2.3 Hz) 2.87 (1 H, ddd, J = 15.7, 5.5, 7.4 Hz)	5.49 (5 H, d, J = 1.4 Hz) 5.42 (5 H, d, J = 1.4 Hz)	1.03 (9 H, s)	270	55.2
3a''	9.88 (1 H, t, J = 8.9 Hz)	3.47 (2 H, d, J = 8.9 Hz)	5.87 (10 H, s)	1.02 (9 H, s)	230	29.4
5	12.04 (2 H, d, J = 6.0 Hz)		5.34 (10 H, d, J = 2.2 Hz)		287	38.1

[a] ^{1}H NMR chemical shift data for the coordinated phosphine or HMPA have been omitted. [b] See ref 8.

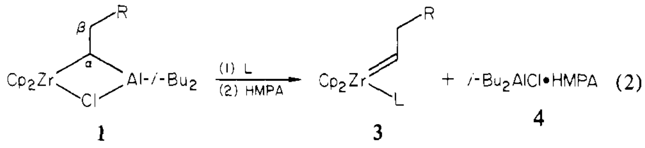
Table II. Product Yields in Alkylidene Transfer Reactions[a]

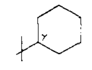
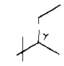
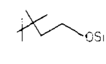
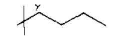


complex	carbonyl compd	product	yield, %
3a	cyclohexanone		≈quantitative
3a	γ-butyrolactone		≈quantitative
3a'			70
3a''			97
3a	methyl benzoate		94
3b	γ-butyrolactone		84
3c	γ-butyrolactone		78
3e	γ-butyrolactone		80

[a] Yields were determined by GLC and are based on **3**.

Table III



complex	R	complex	L	yield, %[a]
1a		**3a**	PPh_3	54
		3a'	PMe_2Ph	70
		3a''	HMPA[b]	69
1b		**3b**	PPh_3	39
		3b'	PMe_2Ph	59
1c		**3c**	PPh_3	33
		3c'	PMe_2Ph	52
1d		**3d**	PMe_2Ph	30
1e		**3e**	PPh_3	8
		3e'	PMe_2Ph	10

[a] See ref 14. [b] No other phosphine ligand added.

groups at the γ position may hamper attainment of a favorable configuration for hydride elimination to aluminum and thus may allow carbene complex formation to compete with it.[17,18]

Zirconium and titanium carbene complexes formed with alkylidene precursors are active "Wittig-type" reagents. Both convert esters to vinyl ethers and ketones to olefins in 78–100% yield.[19] For the Zr compounds the reaction is carried out at 70 °C for 6 h. The more reactive Ti species requires only 2–3 h at room temperature for complete reaction to occur.

Acknowledgment. We acknowledge support for this work by the National Science Foundation and the National Institutes of Health.

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(16) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1973**, *95*, 4451.

(17) In fact, ^{1}H NMR analysis of methine α and β proton splitting patterns for **1a–c**, and **1e** reveals an interesting correlation between the structure of the bridging alkylidene species and the yield of the carbene complex derived from it. For **1a**, H_α is observed as a doublet of doublets ($^3J_{H_\alpha H_\beta}$ = 4.0 Hz, $^3J_{H_\alpha H_{\beta'}}$ = 11.4 Hz), which suggests hindered rotation about the C_α–C_β bond of the alkyl chain. As the size of the alkyl group γ substituent decreases, this splitting pattern evolves toward and then becomes an apparent triplet (for **1b**, $^3J_{H_\alpha H_\beta}$ = 4.0 Hz, $^3J_{H_\alpha H_{\beta'}}$ = 12.0 Hz; for **1e**, $^3J_{H_\alpha H_\beta}$ = 7.3 Hz, $^3J_{H_\alpha H_{\beta'}}$ = 9.2 Hz; for the ethylidene-bridged analogue, a triplet is observed, $^3J_{H_\alpha H_{\beta'}}$ = 8 Hz), consistent with the notion of increasing facility of C_α–C_β bond rotation.

(18) An alternative explanation of the size–yield relationship is that dimerization of the coordinatively unsaturated carbene complex formed by reaction of **1** with HMPA becomes favorable relative to ligand trapping as the steric bulk of the alkyl chain decreases. The observation that the yield of carbene complex does not vary with a 2-fold increase in phosphine ligand trap concentration argues against this hypothesis.

(19) In a typical reaction 1 mmol of a 0.2 M toluene solution of **3a** was added to 1 equiv of a 0.5 M toluene solution of butyrolactone at 50 °C over 10 min. Heating was maintained at 70 °C for 6 h. Workup according to a reported procedure (Pine, S. H.; Zahler, R.; Evans, D. A.; Grubbs, R. H *J. Am. Chem. Soc.* **1980**, *102*, 3270) gave an ethereal solution from which yields were obtained by GLC analysis. Organic products were also isolated and identified by GC–MS and ^{1}H NMR spectroscopy.

Solid-State Rearrangement of (Phenylazophenyl)palladium Hexafluoroacetylacetonate

M. C. Etter* and A. R. Siedle*

Science Research Laboratory
3M Company, St. Paul, Minnesota 55101

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Polymorphic transformations and solid-state chemical reactions, some of them of surprising complexity, are well documented for organic materials,[1] and the scope and importance of organic solid-state chemistry is now well established.[2] Organometallic solid-state reactions have, on the other hand, only rarely been studied.[3] We report a novel rearrangement of (phenylazo-

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(1) (a) Scheffer, J. R. *Acc. Chem. Res.* **1980**, *13*, 283. (b) Paul, I. C.; Curtin, D. Y. *Ibid.* **1973**, *6*, 217.

(2) (a) Gavezzotti, A.; Simonetta, M. *Chem. Rev.* **1982**, *82*, 1. (b) Cohen, M. D.; Green, B. S. *Chem. Br.* **1973**, *9*, 490.

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