vinylcarbene ligand in the present complex may be described as an η^3-bonded one with a strongly coordinated vinyl group.[15]

Reaction of **1d** with cyclopentadiene in THF was completed in 80 min at 40 °C, leading to another 1:1 adduct **4**, a portion of which transformed during chromatography (silica gel/hexane) into the (norbornadiene)$Fe(CO)_3$ derivative **5**, which has a formyl substituent. The isolated yields were 27% and 69%, respectively. In a separate experiment, **4** was converted to **5** quantitatively in 30 min by treatment with a small amount of water and silica gel in hexane at 25 °C. When **4** was oxidatively decomplexed with Me_3NO in acetone, the ethyl ester **6** was obtained as a major product in 48% yield (Scheme II).

The initial product **4** is formulated as an η^4-vinylketene complex by the aid of the above chemical transformations as well as on the basis of spectroscopic analysis. The IR absorption at 1733 cm^{-1} (in CH_2Cl_2) is indicative of a carbonyl group, and the ^{13}C NMR (in C_6D_6) resonance for the carbonyl carbon appears at 231.6 ppm. The other three resonances for the quaternary carbons are observed at 102.5, 86.6, and 32.3 ppm, which are assigned to C(2), C(3), and C(4), respectively, on the η^4-vinylketene moiety.[16] Meanwhile, the ^1H NMR resonances for two vinyl protons at 3.78 and 3.64 ppm indicate coordination of the corresponding carbon–carbon double bond to the iron. Considering the 18-electron rule, the coordination is also inferred from the IR absorptions in the carbonyl region at 2011 and 1957 cm^{-1} and the ^{13}C NMR resonances at 216.9 and 212.6 ppm for two carbonyl ligands.

In (η^3-vinylcarbene)iron(0) complexes analogous to **3**, carbonylation of the carbene carbon, leading to formation of the corresponding (η^4-vinylketene)iron(0) complexes, has been observed under atmospheric CO pressure.[8,17] However, carbonyl–vinylcarbene coupling did not occur in **3** under medium CO pressure (40 psi). Thus, the formation of **4** seems to be promoted by chelation of another internal carbon–carbon double bond as a donor ligand.[18]

A pathway, involving the reverse process of the carbonyl–vinylcarbene coupling, is proposed for the transformation of **4** into **5** in Scheme III: vinylcarbene **8** is generated by decarbonylation of **4** with decomplexation of the carbon–carbon double bond. Protonation on the iron of **8** leads to formation of the cationic iron hydride species **9**, which can be promoted by electron donation from the ethoxy group. Then, reductive elimination is accompanied by detachment of the ethyl group and recoordination of the carbon–carbon double bond to give **5**.

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Supplementary Material Available: Textual presentation of spectral data for **1a–e** and **2–6** and tables of atom coordinates, bond lengths, bond angles, and anisotropic temperature factors for **3** (10 pages); a listing of observed and calculated structure factors for **3** (15 pages). Ordering information is given on any current masthead page.

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(15) Nakatsu, K.; Mitsudo, T.; Nakanishi, H.; Watanabe, Y.; Takegami, Y. *Chem. Lett.* **1977**, 1447–1448.

(16) The assignment is consistent with that for the analogous (η^4-vinylketene)iron(0) complex, which appears in ref 8. For other (η^4-vinylketene)iron(0) complexes, see: Alcock, N. W.; Richards, C. J.; Thomas, S. E. *Organometallics* **1991**, *10*, 231–238 and references therein.

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(18) There is an example for carbonyl–vinylcarbene coupling by addition of chelating donor ligands: Myar, A.; Asaro, M. F.; Glines, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 2215–2216.

Solid-State Organometallic Chemistry of Tripodal (Polyphosphine)metal Complexes. C–H Activation Reactions at Cobalt(I) Encapsulated into the Tetraphosphine $P(CH_2CH_2PPh_2)_3$

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Summary: The solid–vapor reactions of $[(PP_3)Co(N_2)]BPh_4$ with HC≡HC, $H_2C{=}CH_2$, CH_2O, MeCHO, and CO are described ($PP_3 = P(CH_2CH_2PPh_2)_3$). The organic molecules either displace N_2, forming a 1:1 complex, or undergo C–H bond cleavage at cobalt to give intermediates that may optionally eliminate H_2 or promote hydrogen transfer from metal to coordinated organic ligand.

Little attention has been given to solid-state organometallic chemistry, essentially limited to the reactions of interstitial $[(PPh_3)_2Ir(H)_2]^+$ in lattices comprised of anionic metal oxide clusters.[1]

In this communication, we describe studies designed to exploit some unique features of the tetraphenylborate salts of tripodal (polyphosphine)metal complexes in the solid–vapor reactions with small organic molecules. We report here preliminary data on the reactions of $[(PP_3)Co(N_2)]BPh_4$ (**1**)[2] with HC≡HC, $H_2C{=}CH_2$, CH_2O, MeCHO, and CO ($PP_3 = P(CH_2CH_2PPh_2)_3$).

Compound **1** appears as purple-red crystals, quite stable in the solid state under argon or under reduced pressure (0.1 Torr) at 100 °C. Differential scanning calorimetry (DSC) shows no phase change up to 173 °C, at which temperature the compound begins to melt with decomposition. The complex cation in **1** exhibits trigonal-bipyramidal geometry in both the solid state[3] and solution[2] with

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(1) (a) Siedle, A. R.; Newmark, R. A. *Organometallics* **1989**, *8*, 1442. (b) Siedle, A. R.; Newmark, R. A. *J. Am. Chem. Soc.* **1989**, *111*, 2058. (c) Siedle, A. R.; Newmark, R. A.; Sahyun, M. R. V.; Lyon, P. A.; Hunt, S. L.; Skarjune, R. P. *J. Am. Chem. Soc.* **1989**, *111*, 8346.

(2) Bianchini, C.; Mealli, C.; Meli, A.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1988**, *110*, 8725.

(3) Crystal data: monoclinic, space group $P2_1/n$, a = 13.049 (2) Å, b = 35.635 (4) Å, c = 13.154 (1) Å, β = 100.31 (1)°, d_{calcd} = 1.23 g cm^{-3}, Z = 4, n_{obsd} = 2876, R = 0.087. Selected bond distances (Å) and angles (deg): $Co{-}P_{equatorial}$ (av) = 2.230 (5), $Co{-}P_{apical}$ = 2.146 (4), Co–N = 1.86 (1), N–N = 1.08 (2); $P_{apical}{-}Co{-}N$ = 176.3 (4), Co–N–N = 178.1 (1).

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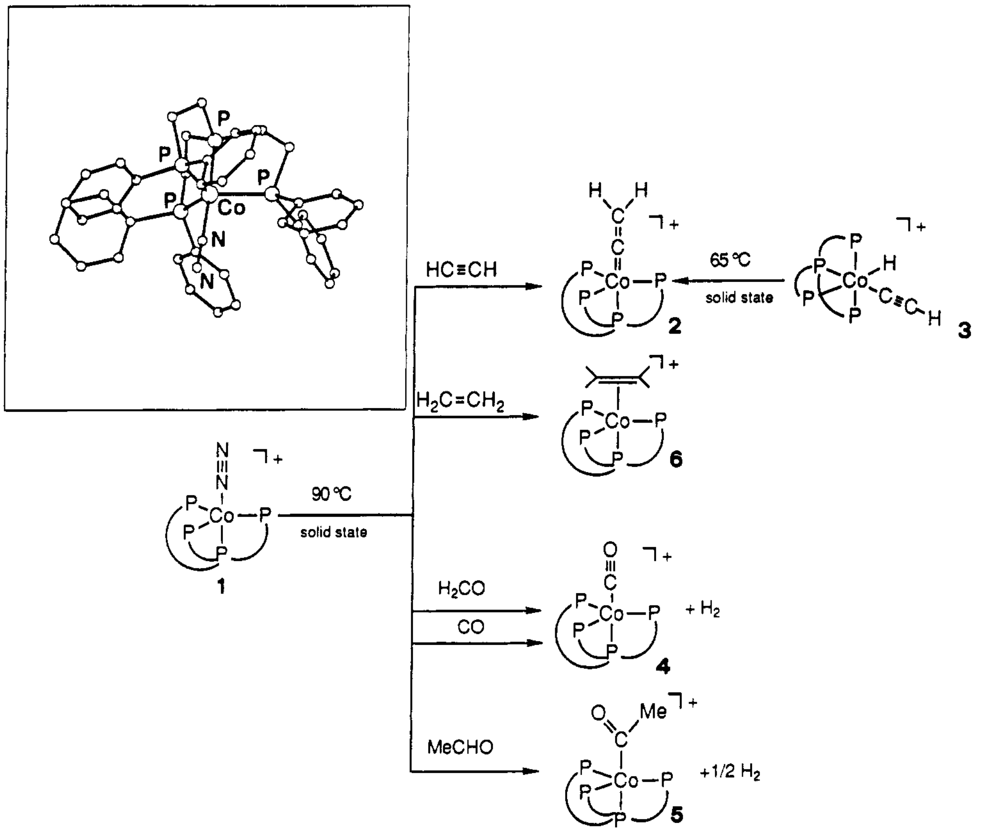
Scheme I



the dinitrogen ligand in the axial position trans to the bridgehead phosphorus of PP_3.

In a typical experiment, a gaseous molecule is passed over crystals of 1 for 2 h at 90 °C. As a result, N_2 is evolved and a 1:1 complex involving the two reagents is formed as shown by a clear-cut color change (Scheme I). Termination of every reaction is determined by the disappearance of the IR stretching band of the N≡N bond (2125 cm^{-1}). The complexes formed were authenticated by comparing their IR (KBr), ^{31}P, ^{1}H, and ^{13}C NMR, ESR, and UV-vis spectra with those of authentic samples prepared in tetrahydrofuran (THF) solution by reacting 1 with the appropriate organic substrate. All of the solid-state reactions exhibit high yields (90–100%), thus indicating that almost all cobalt centers are accessible to the organic molecules.

No appreciable fragmentation of the crystals of the precursor is observed, indicating that the reactions do not proceed by interaction of the organic molecules with the surface of 1, followed by breaking up the crystal structure to facilitate further migration and reaction. On the other hand, the products appear slightly opaque and the single-crystal nature is lost, as shown by observation with a cross-polarizing microscope. Interestingly, a crystalline structure is maintained in the product of the reaction with ethyne, which, by the way, involves complicated chemistry: acetylene to vinylidene tautomerization, a reaction that requires a much higher temperature (ca. 500–600 °C) in the absence of a metal promoter.[4] The purple vinylidene complex that forms, $[(PP_3)Co(C{=}CH_2)]BPh_4$ (2), can be prepared also by heating a THF solution of the Co(III) complex $[(PP_3)Co(H)(C{\equiv}CH)]BPh_4$ (3) at 50 °C (formal 1,3-H shift).[5] Accordingly, one might reasonably conclude that also the solid-state acetylene to vinylidene rearrangement proceeds via a hydride alkynyl intermediate. Indeed, when a solid sample of 3 is heated under argon at 65 °C, we observe its quantitative conversion to 2. All our attempts to trap eventual intermediates during the straightforward solid-state conversion of HC≡CH to $C{=}CH_2$ at cobalt were unsuccessful, probably due to the temperature required to promote the reaction (solid 1 is stable under a stream of C_2H_2 below 65 °C). Actually, were a hydride alkynyl complex on the way to being formed, it would not be possible to isolate it because, at the experimental temperature (90 °C), it readily rearranges to vinylidene 2.

Formaldehyde is decomposed to H_2 (detected by GC) and CO, the latter fragment being trapped by the metal to give the yellow carbonyl $[(PP_3)Co(CO)]BPh_4$ (4),[6] obtainable also by the straightforward reaction of solid 1 with CO. The reaction with CH_2O can be interpreted as a typical oxidative-addition/reductive-elimination path, involving no change of the formal oxidation state of the metal.[7] In contrast, the reaction between 1 and MeCHO gives the *paramagnetic* Co(II) σ-acyl complex $[(PP_3)Co(COMe)]BPh_4$ (5;[8] low-spin d^7 configuration, $\mu_{eff} = 2.15\ \mu_B$) and H_2 and, therefore, suggests the occurrence of homolytic splitting of the Co–H bond after oxidative addition.[7] Whether H migrates through the crystal lattice to react with another H• or C–H bond is not possible to assess at

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[4] (a) Duran, R. P.; Amorebieta, V. T.; Colussi, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 3154. (b) Stang, P. J. *Chem. Rev.* **1978**, *78*, 383. For a theoretical approach to this problem see: Gallo, M. M.; Hamilton, T. P.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1990**, *112*, 8714.

[5] Bianchini, C.; Peruzzini, M.; Vacca, A.; Zanobini, F. *Organometallics*, in press.

[6] Ghilardi, C. A.; Midollini, S.; Sacconi, L. *Inorg. Chem.* **1975**, *14*, 1790.

[7] Bianchini, C.; Meli, A. *Organometallics* **1985**, *4*, 1537.

[8] 5: IR (KBr) 1620 cm^{-1} (ν(C═O), s) 1310 cm^{-1} (ν(C—O—C), m); $\mu_{eff} = 2.15\ \mu_B$ (Faraday balance); diffuse-reflectance spectrum at 20 °C, 9259, 16666 (sh), 21276 cm^{-1}. Anal. Calcd for $C_{68}H_{65}BCoOP_4$: C, 74.80; H, 6.00; Co, 5.40. Found: C, 74.27; H, 5.89; Co, 5.23.

this stage. We have found that the reaction occurs also in the dark. In THF solutions, 1 reacts with MeCHO at room temperature, producing **5** and H_2. Variable-temperature $^{31}P\{^1H\}$ NMR studies show the existence of a diamagnetic intermediate species in the range −60 to −40 °C exhibiting an AM_3 spin system (at −60 °C, $\delta(P_{apical})$ 146.5, $\delta(P_{equatorial})$ 55.4, $J(PP) = 29.8$ Hz). At higher temperature, this species rapidly decomposes to the paramagnetic σ-acyl **5**. The NMR pattern is typical for trigonal-bipyramidal Co(I) complexes of the formula $[(PP_3)CoL]$,[2] and therefore, one may reasonably suggest the formation of a kinetic product containing intact MeCHO coordinated via the C=O group in either η^2(C,O) or η^1(O) bonding modes.[9] Unfortunately, the poor stability of the complex has not allowed us to isolate it.

The only reversible reaction is the one with ethylene, affording the yellow orange π-ethylene complex $[(PP_3)Co(C_2H_4)]BPh_4$ (**6**),[10] which converts to the precursor **1** under a stream of N_2 at 90 °C.

In light of the fact that the loss of the N_2 ligand from **1** is induced by neither heat nor vacuum, we propose that this chemistry readily occurs in the solid state because the phosphine arms of PP_3 have sufficient motional freedom in the lattice at 90 °C to permit access to small organic molecules. Such a motion may involve either unfastening of a phosphine arm of PP_3[11] or a simple opening of a P–Co–P angle in the equatorial plane of the trigonal bipyramid. Interestingly, below 90 °C no appreciable reaction occurs between **1** and organic molecules, suggesting the existence of a thermal barrier to the creation of a coordination site at the metal.

The small organic molecules could penetrate the crystals of **1**, dissolving in the extensive hydrophobic region comprised of ten phenyl substituents and six methylenic groups per molecule.[1] As a matter of fact, the substitution of BF_4^-, PF_6^-, or $SO_3CF_3^-$ for BPh_4^- in **1** significantly lowers the yields of the solid–vapor reactions involving CH_2O and C_2H_2, whereas no reaction occurs with MeCHO and C_2H_4. The larger size of the tetraphenylborate counteranion, causing larger channels in the crystal lattice, could play a role in determining the selectivity of the reactions.

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Supplementary Material Available: Text describing experimental details, syntheses, and characterization of $[(PP_3)Co(C{=}CH_2)]BPh_4$, $[(PP_3)Co(H)(C{\equiv}CH)]BPh_4$, $[(PP_3)Co(C_2H_4)]BPh_4$, and $[(PP_3)Co(COMe)]BPh_4$ and X-ray crystallographic data for **1**·0.5THF, including a labeled PLUTO drawing, experimental details (Table I), selected distances and angles (Table II), and atomic coordinates and thermal parameters (Table III) (8 pages); a listing of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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[9] Mendez, N. Q.; Arif, A. M.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1473.

[10] **6**: $^{31}P\{^1H\}$ NMR (121.42 MHz, acetone-d_6), AM_3 spin system temperature-invariant spectrum from −80 to +30 °C, at −70 °C $\delta(P_A)$ 162.63, $\delta(P_M)$ 70.78, $J(P_AP_M) = 47.21$ Hz; ^1H NMR (299.946 MHz, acetone-d_6, 20 °C) $\delta(C_2H_4)$ 2.99 ppm, br quartet, $J(HP_{terminal}) = 4.9$ Hz. Anal. Calcd for $C_{68}H_{66}BCoP_4$: C, 75.85; H, 6.18; Co, 5.46. Found: C, 75.13; H, 6.20; Co, 5.54.

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Formation of Ion Pairs in the Ziegler Ethylene Polymerization Catalyst System $Cp_2Ti(Cl)CH_2SiMe_3–AlCl_3$[1]

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Summary: Monitoring the interaction of ((trimethylsilyl)methyl)titanocene chloride with aluminum chloride in polar halocarbons by ^1H, ^{13}C, and ^{27}Al NMR spectroscopy has yielded direct spectral evidence for the generation of equilibrating solvent-separated and contact ion pairs, $Cp_2Ti(CH_2SiMe_3)^+$ and $AlCl_4^-$. Such ion pairs are effective catalysts for the polymerization of ethylene, and as required by this action, Me_3Si fragments from the titanocene component are incorporated into the linear, high-density polyethylene formed. X-ray diffraction data on ((trimethylsilyl)methyl)titanocene chloride (space group $P2_1/n$; $R = 0.042$; $R_w = 0.050$; $\rho(\max) = 0.43$ e/Å^3) reveal an unusually short Ti–CH_2 bond (2.162 Å) and an anti conformational arrangement of the Me_3SiCH_2 group with the Ti–Cl bond.

In recent studies of soluble Ziegler catalysts[2] for the polymerization of ethylene,[3] we had obtained indirect evidence that such titanium–aluminum cocatalytic combinations generate ionic organotitanium intermediates that are the actual active polymerization sites.[4-6] Subsequently, excellent investigations of other groups, such as those of Jordan, Marks, Bochmann, and Taube, have lent strong corroboration to this viewpoint and have shown its applicability to zirconium-catalyzed polymerizations as

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[1] Organometallic Compounds of Group III. 47. Part 46: Eisch, J. J.; Caldwell, K. R. *New Science in Transition Metal Catalyzed Reactions*; Advances in Chemistry 230; American Chemical Society: Washington, DC, in press.

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[3] Homogeneous titanium catalysts for the polymerization of ethylene are customarily termed Ziegler catalysts (Long, W. P. *J. Am. Chem. Soc.* 1959, *81*, 5312), while heterogeneous titanium catalysts for polymerizing ethylene and 1-alkenes are called Ziegler–Natta catalysts.

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