nonidentical, as shown by the clearly differentiated δ values of 10.2 and 9.39, which suggests hydrogen bonding between the peri carbonyl and the proximate exocyclic N–H. The UV spectrum (EtOH) was indicative of the extended ring system: λ_{max} (ϵ) 331 (9500), 309 (8700), 253 sh (7200), 245 sh (9800).

While the analytical and spectroscopic data were consistent with proposed structure **2**, they were not completely definitive for distinguishing it from the three other possible isomeric products arising from different modes of condensation–cyclization of **1** (**1**-N^2 vs. N^2-**3**) and **3** (C=N vs. C≡N). Therefore, we obtained confirmation of structure **2** by a pair of parallel spectroscopic matches involving **2** and its 2-bromo derivative with the product of 9-benzylguanine[20] with **3** and its corresponding bromo derivative. Single-crystal X-ray analysis showed the presence of two crystallographically independent molecules in the solid-state structure of 8-amino-3-benzyl-2-bromo-9,10-dihydro-10-oxo-3*H*-1,3,5-triazino[1,2-*a*]purine ($C_{14}H_{10}BrN_7O$),[19] mp 282–284 °C dec.[21] Molecules **4a** and **4b** in Figure 1 are nearly planar through the entire tricyclic base moiety.

IA′-Metamorphosine (**2**) exhibits fluorescence on a TLC plate (silica gel); however, in aqueous solution at 20 °C, Φ is only 0.003 (compared with rhodamine G) for $\lambda_{max}{}^{ex}$ 350 nm, $\lambda_{max}{}^{em}$ 361–590 nm (br), and τ (by phase) = 0.38 ns. In glycerol at 20 °C, by contrast, $\Phi = 0.19$, $\lambda_{max}{}^{em}$ 444 nm, $\tau = 1.31$ ns (by phase), and 1.38 ns (by modulation), and at −38 °C, $\Phi = 0.985$ and $\lambda_{max}{}^{em}$ 450 nm. These changes probably reflect a change in the facility of adiabatic proton transfer from NH_2 to the peri carbonyl as well as a decrease in energy release via vibrational processes. The reagent described herein, methyl *N*-cyanomethanimidate and NaOMe in methanol, has potential application as a spray reagent for thin-layer or paper chromatography. Observed fluorescence develops on heating a sprayed chromatogram at the location of guanosine and adenosine but not at cytidine or uridine. Since only adenine- or adenosine-containing compounds react with chloroacetaldehyde as a spray reagent to develop fluorescence,[22] the two spray reagents can be used in parallel for full differentiation. IA′-Metamorphosine functions as a competitive inhibitor, $K_i = (2.3 \pm 0.3) \times 10^{-4}$, of adenosine with adenosine deaminase.[23] It is nonmutagenic in the bacterial mutagen (Ames) screening test.[24]

Compound **2** can serve also as a "protected" guanosine (**1**) since quantitative reconversion of **2** to **1** occurs upon treatment with 0.1 N NaOH at 20 °C within 5 min. The modification of guanosine to an N-tricyclic derivative, as in **2**, by means of methyl *N*-cyanomethanimidate and nonaqueous base, can be extended to other guanine-containing substrates.

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Registry No. 1, 118-00-3; **2**, 92220-57-0; **3**, 51688-22-3; **4**, 58-61-7.

Supplementary Material Available: Complete crystallographic data for 8-amino-3-benzyl-2-bromo-9,10-dihydro-10-oxo-3*H*-1,3,5-triazino[1,2-*a*]purine (**4a,b**), including tables listing atomic positional and thermal parameters, bond angles, torsional angles, intermolecular contact distances, weighted least-squares planes, and observed and calculated structure factors (44 pages). Ordering information is given on any current masthead page.

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(Trimethylphosphine)cobalt(I) Complexes. 3. $Co(PMe_3)_2(BPh_4)$, the First Structural Example of Tetraphenylborate Anion π-Coordinated to a First-Row Metal Ion

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The tetraphenylborate anion is widely used as an "inert" counterion to isolate cationic species from solutions. However, its role is sometimes not as passive as those of the perchlorate, tetrafluoroborate, or hexafluorophosphate anions, since it can coordinate to transition metals via π-bonded interaction with one of its phenyl groups.[2,3] This type of bonding has been observed for $ML_2(BPh_4)$ complexes (M = Rh(I) and Ir(I) and L = diene, PR_3, etc.).[4] The presence of a π-bonded BPh_4^- group has been shown by X-ray diffraction for $Rh(P(OMe)_3)_2(BPh_4)$[5] and, more recently, for the analogous compounds in which the phosphites are replaced by a bidentate diphos ligand.[6] The Rh(I) and Ir(I) compounds are known as inert d^8 compounds with low, if any, catalytic activity.[7]

During our investigation of the basic chemistry of Co^I–PR_3 systems, it appeared to us that such complexes are also present when $CoX(PR_3)_3$ compounds are reacted in presence of $NaBPh_4$. The only reported Co(I) complex of this type, $Co(P(OEt)_3)_2(BPh_4)$, has been synthesized by this method.[8] The chemical and structural characterization of the trimethylphosphine complex $Co(PMe_3)_2(BPh_4)$ is herein reported.

Addition of sodium tetraphenylborate to a methanol or acetone solution of $CoBr(PMe_3)_3$ gives rise to two species, $[Co(PMe_3)_4]BPh_4$ and $Co(PMe_3)_2(BPh_4)$, according to reaction 1. They were separated by fractional crystallization.

$$2CoBr(PMe_3)_3 + 2NaBPh_4 \rightarrow [Co(PMe_3)_4]BPh_4 + Co(PMe_3)_2(BPh_4) + 2NaBr \quad (1)$$

$[Co(PMe_3)_4]BPh_4$, obtained as blue-green crystals, is a paramagnetic tetracoordinate species ($\mu_{eff} = 2.8\ \mu_B$ at 295 K). Its X-ray structure[9] indicates a distorted tetrahedral coordination with normal Co–P bonds (av 2.227 Å) and one P–Co–P angle (125.4 (1)°) noticeably greater than the other five (101.1 (1)–113.1 (1)°). A similar structure has been observed for the d^9 $[Ni(PMe_3)_4]BPh_4$ compound.[11] The geometry of the BPh_4^- ion is normal.

Dark brown crystals of the diamagnetic $Co(PMe_3)_2(BPh_4)$ complex can be handled in air without transformation into phosphine oxide complexes. They are reasonably stable in acetone

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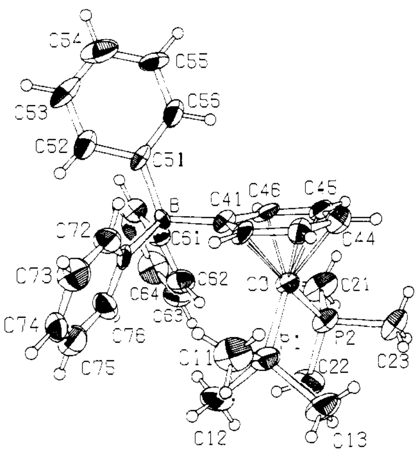

Figure 1. ORTEP drawing of the $Co(PMe_3)_2(BPh_4)$ molecule. Ellipsoids correspond to 50% probability. Hydrogens are represented as spheres of arbitrary size. Distances: Co–P1, 2.171 (3); Co–P2, 2.164 (3); Co–C41, 2.219 (9); Co–C42, 2.096 (9); Co–C43, 2.131 (11); Co–C44, 2.123 (12); Co–C45, 2.119 (10); Co–C46, 2.120 (9); Co–centroid, 1.602 Å. Angles: P1–Co–P2, 94.6 (1)°; P1–Co–centroid, 133.5°; P2–Co–centroid, 131.7°.

or dichloromethane solutions. X-ray diffraction[12] shows that they consist of monomeric molecules (Figure 1) in which the Co(I) center is σ-bonded with two PMe_3 ligands and π-bonded with one of the phenyl rings of the BPh_4^- ion. The Co–P distances (av 2.167 (3) Å) are normal. The C–C distances in the π-bonded ring (av 1.412 Å) are longer than those of the free rings (av 1.386 Å) as a result of metal-to-ligand back-bonding. The π-bonded ring is planar, except for the Ph_3B-bonded carbon, which is displaced by 0.044 Å from the plane of the remaining five carbon atoms, away from cobalt. This ring distortion, which probably minimizes steric hindrance, is different from those previously found. Except for this carbon, the Co–C distances (2.096 (9)–2.131 (11) Å, av 2.118 Å) are equal, indicating that the ring behaves as a normal 6-electron donor. Therefore, $Co(PMe_3)_2(BPh_4)$ can be regarded as an 18-electron system.

Its $^{31}P\{^1H\}$ spectrum at 295 K shows no signal as commonly found for Co–PMe_3 complexes.[16] At 183 K, a broad singlet is present at 8.3 ppm, which is consistent with two equivalent phosphorus atoms.[13] The ^{13}C and $^{13}C\{^1H\}$ spectra at 295 K exhibit only a small ill-resolved signal at 19 ppm, corresponding to the P-bonded methyl groups. At 223 K, however, well-resolved spectra are obtained, and decreasing the temperature has no supplementary effect on the spectra. Figure 2 shows the 183 K $^{13}C\{^1H\}$ spectrum in CD_2Cl_2. The ^{13}C data are consistent with the X-ray result. The five coplanar carbon atoms of the π-bonded ring are shifted upfield as expected, but only a small downfield shift is observed for the Ph_3B-bonded carbon, which is certainly related to the presence of a positive charge on the adjacent boron atom. The $^1H\{^{31}P\}$ spectrum is temperature dependent and indicates that a complicated exchange process is occurring between the hydrogens of the phenyl groups. At 183 K, exchange is still present, but two broad singulets are resolved at 5.0 and 5.3 ppm, in the range where the protons of the coordinated phenyl ring are expected. The last protons are probably masked by the broad signal at ~7 ppm for the free phenyl ring.

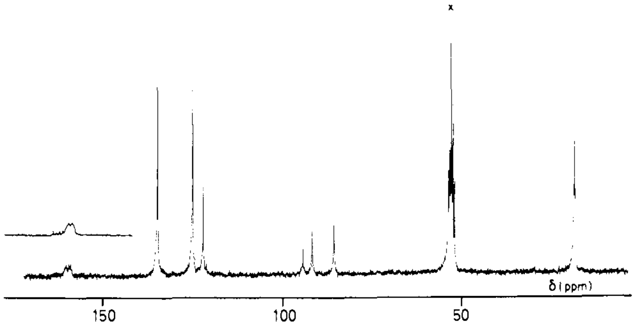

Figure 2. $^{13}C\{^1H\}$ spectrum, 183 K, of a CD_2Cl_2 solution of $Co(PMe_3)_2PBh_4$ ($\delta(SiMe_4) = 0$) PMe_3, 20 ($J_{CH} = 126$, $J_{CP} = 15$ Hz); uncoordinated Ph, 123 ($J_{CH} = 159$ Hz), 125 ($J_{CH} = 155$ Hz), 135 ($J_{CH} = 153$ Hz), 159.5 (J_{CB} = unresolv.); coordinated Ph, 86 ($J_{CH} = 163$ Hz), 92 ($J_{CH} = 163$ Hz), 95 ($J_{CH} = 160$ Hz), 162.5 ($J_{CB} = 50$ Hz) (x = CD_2Cl_2).

$Co(PMe_3)_2(BPh_4)$ is not inert toward nucleophilic substitution in contrast with the rhodium complexes. In solution, the Co–(C_6H_5) π-bond is easily broken in the presence of nucleophiles such as PMe_3, CO, ethylene, or acetylene. Investigations in this direction are in progress since we have at hand the reactive 12-electron $[Co(PMe_3)_2]^+$ moiety, which until now has been stabilized and studied only as cyclopentadienyl[14] or carbonyl species.[15]

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Registry No. $[Co(PMe_3)_4]BPh_4$, 53432-11-4; $Co(PMe_3)_2(BPh_4)$, 92220-66-1; $CoBr(PMe_3)_3$, 53432-07-8; $NaBPh_4$, 143-66-8.

Supplementary Material Available: Refined atomic coordinates and temperature factors for $[Co(PMe_3)_4]BPh_4$ and $Co(PMe_3)_2(BPh_4)$ (8 pages). Ordering information is given on any current masthead page.

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[12] $Co(PMe_3)_2(BPh_4)$ is monoclinic, $P2_1/c$, $a = 11.457$ (3) Å, $b = 13.804$ (4) Å, $c = 19.339$ (8) Å, $\beta = 115.21$ (3)°, $Z = 4$. Structure refined on 2857 Cu Kα reflections ($I > 3\sigma(I)$)[10] to $R = 0.051$ and $R_w = 0.052$.

[13] The $^1H\{^{31}P\}$, ^{13}C, $^{13}C\{^1H\}$, and $^{31}P\}^1H\}$ NMR spectra were recorded at 250 MHz for ^1H, 101.27 MHz for ^{31}P, and 62.9 MHz for ^{13}C, with a Bruker WM-250 spectrometer.

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Novel Suicide Inhibitors of Serine Proteinases. Inactivation of Human Leukocyte Elastase by Ynenol Lactones†

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There has been considerable interest in developing specific proteinase inhibitors as pharmacological and therapeutic agents.[1-4] Scheme I depicts a strategy for serine proteinase inhibition, in which a new class of compounds, the ynenol lactones, are featured

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