$(\eta^5\text{-}C_5H_5)Cr(NO)_2^+$ product and the neutral hydrido complex $(\eta^5\text{-}C_5H_5)Cr(NO)_2H$. However, this latter compound is thermally unstable[32] and reverts to the original dimeric reactant via eq 18. Sequential recycling of conversions

$$2(\eta^5\text{-}C_5H_5)Cr(NO)_2H \xrightarrow{CH_2Cl_2} [(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2 + H_2 \tag{18}$$

13, 17, and 18 finally results in the net transformation (2) which is observed experimentally. In a similar manner when M = Mn, the initial $[(\eta^5\text{-}C_5H_4R)Mn(CO)(NO)]_2H^+$ adduct could cleave in a number of ways. One such unsymmetrical cleavage would produce the observed $[(\eta^5\text{-}C_5H_4R)Mn(CO)_2(NO)]^+$ cations and $(\eta^5\text{-}C_5H_4R)Mn(NO)H$, the latter complexes being logical precursors for the trimetallic reactants of reaction 12. Nevertheless, the origins of the bimetallic nitrosyl products presented in Scheme II remain to be ascertained, reactions 10 and 11 being unlikely in this system.

One final point merits mention. In principle, the initial cationic adducts formed via reaction 13 could also undergo inner-sphere electron-transfer processes, i.e., eq 19, the net

$$[(\eta^5\text{-}C_5H_4R)M(LO)_2]_2H^+ \xrightarrow{CH_2Cl_2} [(\eta^5\text{-}C_5H_4R)M(LO)_2]_2^+ + {}^1/{}_2H_2 \tag{19}$$

result being formation of the bimetallic monocations. We have not found any direct physical evidence for the existence of such bimetallic species in the iron, chromium, or manganese systems. Interestingly, however, we have observed this to be the principal mode of reaction when $[(\eta^5\text{-}C_5H_5)Co(NO)]_2$ is treated with a slight excess of $HBF_4{\cdot}OMe_2$ in CH_2Cl_2, i.e., eq 20. The previously reported,[33] paramagnetic $[(\eta^5\text{-}C_5H_5)Co(NO)]_2BF_4$ may be easily isolated as a purple microcrystalline solid in 73% yield from the final reaction mixture.

$$[(\eta^5\text{-}C_5H_5)Co(NO)]_2 + HBF_4{\cdot}OMe_2 \xrightarrow{CH_2Cl_2} [(\eta^5\text{-}C_5H_5)Co(NO)]_2BF_4 + {}^1/{}_2H_2 + OMe_2 \tag{20}$$

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Registry No. $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4H]BF_4$, 86365-53-9; $[\{(\eta^5\text{-}C_5H_5)Cr(NO)_2\}_2OH]BF_4$, 86365-55-1; $(\eta^5\text{-}C_5H_5)Cr(NO)_2(OHBPh_3)$, 86365-56-2; $(\eta^5\text{-}C_5H_5)Cr(NO)_2Br$, 77662-15-8; $[\{(\eta^5\text{-}C_5H_5)Cr(NO)_2\}_2OH]BPh_4$, 86365-57-3; $(\eta^5\text{-}C_5H_5)_2Mn_2(NO)_3(NO_2)$, 36534-34-6; $[(\eta^5\text{-}C_5H_5)_3Mn_3(NO)_3(NH)]BF_4$, 86365-59-5; $[(\eta^5\text{-}C_5H_5)_2Mn_2(NO)_2(CO)(NH_2)]BPh_4$ (cis isomer), 86365-61-9; $(\eta^5\text{-}C_5H_4Me)_2Mn_2(NO)_3(NO_2)$, 75847-53-9; $[(\eta^5\text{-}C_5H_4Me)_3Mn_3(NO)_3(NH)]BF_4$, 85649-58-7; $[(\eta^5\text{-}C_5H_4Me)_2Mn_2(NO)_2(CO)(NH_2)]BPh_4$ (cis isomer), 86365-63-1; $[(\eta^5\text{-}C_5H_5)Co(NO)]_2BF_4$, 84577-24-2; $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, 12154-95-9; $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$, 36607-01-9; $[(\eta^5\text{-}C_5H_5)Mn(CO)(NO)]_2$, 69120-59-8; $[(\eta^5\text{-}C_5H_5)Co(NO)]_2$, 51862-20-5; $[(\eta^5\text{-}C_5H_5)_2Mn_2(NO)_2(CO)(NH_2)]BPh_4$ (trans isomer), 86391-48-2; $(\eta^5\text{-}C_5H_4Me)_2Mn_2(NO)_2(CO)(NH_2)]BPh_4$ (trans isomer), 86391-50-6.

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Communications

Catalytic Effect of Bases on the Formation of $HCo(CO)_4$ from $Co_2(CO)_8$ and H_2

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Summary: The hydrogenation of $Co_2(CO)_8$ to $HCo(CO)_4$ is catalyzed by tertiary amines, nitrogen heterocycles, tertiary phosphorus bases (with $pK_a \geq 5$), and halide ions. For example, with 28 mol % of pyridine based on $Co_2(CO)_8$, the rate of $HCo(CO)_4$ formation may be increased about 300-fold at 40 °C.

The stoichiometric reaction of $HCo(CO)_4$ with olefins to yield aldehydes proceeds smoothly at room temperature and atmospheric pressure.[1,2] However, cobalt-catalyzed hydroformylation is generally carried out at high pressures and temperatures.[3] Obviously, only the formation of $HCo(CO)_4$ from $Co_2(CO)_8$ by H_2 needs drastic conditions. Consequently the catalytic hydroformylation should be possible under much milder conditions if the very slow hydrogenation of $Co_2(CO)_8$ to $HCo(CO)_4$ could be accelerated.[4]

The effect of bases on hydroformylation was already the subject of numerous studies. Experiments were carried out under "hydroformylation conditions", and in most cases an inhibition or only a moderate activation was found.[3,5] The most detailed study was carried out by Iwanaga,[6] who observed that the effect of nitrogen bases depends on their basicity, pyridine and its derivatives giving the best results. In all these works, however, relatively large amounts of additives were used (above 1 mol/mol Co) which inevitably leads to $[Co(CO)_4]^-$ formation due to the disproportionation of $Co_2(CO)_8$.[7] Since

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Table I. Hydrogenation of $Co_2(CO)_8$ in the Presence of Various Additives[a]

no.	additive[b]	$[HCo(CO)_4]$, % of Co	no.	additive	$[HCo(CO)_4]$, % of Co
1	none	<0.5	19	NH_2Pr	1.9
2	none[c]	9.3	20	bpy[d]	1.4
3	MeOH	<0.5	21	phen[d]	6.7
4	Me_2CO	<0.5	22	dmgH[d]	1.0
5	Et_2O	<0.5	23	PPh_3	1.4
6	MeCN	<0.5	24	PPh_2Me	1.4
7	dmf	2.6	25	diphos[d]	15.7
8	quin	14.8	26	PBu_3	17.1
9	8-OHquin	18.6	27	$PMe(i\text{-}Pr)_2$	18.6
10	py	17.6	28	$P(i\text{-}Pr)_3$	14.5
11	2-Mepy	17.9	29	P(c-Hx)	20.0
12	$2,4\text{-}Me_2py$	16.7	30	$P(OPh)_3$	0.7
13	$2,6\text{-}Me_2py$	<0.5	31	$P(OBu)_3$	12.9
14	NMe_2Ph	6.2	32	$AsPh_3$	2.1
15	NEt_3	3.3	33	$SbPh_3$	<0.5
16	$N(CH_2CH_2OH)_3$	<0.5	34	$K_2[CoCl_4]$[d-f]	21.6
17	$NH(CH_2CH_2)_2O$	1.4	35	$K_2[CoBr_4]$[d-f]	18.8
18	$NH(CH_2)_5$	1.7	36	$K_2[CoI_4]$[d-f]	15.2

[a] Reaction conditions: 50 °C, p_{H_2} = 70 bar, p_{CO} = 5 bar, toluene solution $[Co_2(CO)_8]$ = 0.105 M, [additive] = 0.011 M, reaction time 30 min. [b] Key to abbreviations: dmf, *N,N*-dimethylformamide; quin, quinoline; py, pyridine; bpy, 2,2'-bypyridine; phen, 1,10-phenantroline; dmgH, diacetyl dioxime; diphos, 1,2-bis(diphenylphosphino)ethane. [c] Reaction time 6 h. [d] [Additive] = 0.006 M. [e] In CH_2Cl_2 solution. [f] K^+ ions were solvatized by 18-crown-6, see ref 12.

$[Co(CO)_4]^-$ is catalytically inactive, this side reaction further complicates the interpretation of the effect of bases on hydroformylation. Consequently no competent explanation has been offered up till now for this base effect.

We now investigated the effect of catalytic amounts of various bases on the hydrogenation of $Co_2(CO)_8$. The following general procedure was used. A Teflon-coated stainless-steel autoclave (10 cm^3) was flushed with argon. A 3.0-cm^3 sample of $Co_2(CO)_8$ stock solution in toluene (0.21 M) and 0.063 mmol of the additive (in the most cases in form of a 1.24 M stock solution in toluene) were added, and the volume of the reaction mixture was completed to 6.0 cm^3 with toluene. The autoclave was closed quickly, flushed with a gas mixture H_2/CO = 70/5, and pressurized up to 75 bar with the same gas mixture. The autoclave was thermostated at 50 °C, shaken for 30 min, and cooled to −78 °C for 30 min. After the pressure was released, the concentration of $HCo(CO)_4$ in the product was determined by the methylene blue titration method of Iwanaga.[8] The $[Co(CO)_4]^-$ content of the reaction mixture was determined by means of IR analysis and if necessary, used to correct the result of the titration.

Oxygen bases and nitrogen bases containing mobile protons had only a slight effect on the reaction, but in the case of some nitrogen heterocycles and tertiary phosphines a strong catalytic effect was found (Table I). In addition, halide ions catalyzed the reaction as well.

The relative concentration of three additives was varied between 0.7 and 100 mol % based on $Co_2(CO)_8$. In all cases $HCo(CO)_4$ concentration showed a maximum as a function of the ratio lg ([additive]/[Co])[9] (Figure 1). This maximum was very sharp in the case of pyridine at lg ([py]/[Co]) = −0.85 (~28 mol % of pyridine based on $Co_2(CO)_8$). Preliminary kinetic experiments performed at 40 °C and 50-bar total pressure showed that the initial rate of $HCo(CO)_4$ formation was increased at least 300-fold by the addition of this amount of pyridine as compared to the rate observed in the absence of any additive.

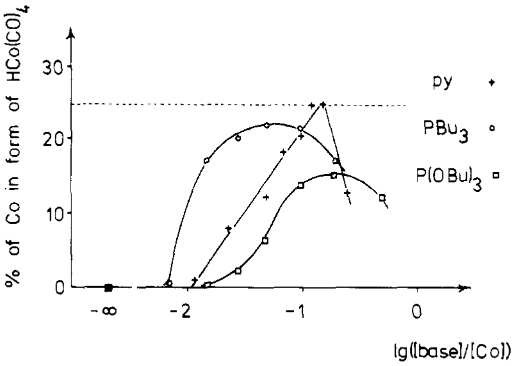

Figure 1. $HCo(CO)_4$ concentration as a function of base concentration. Reaction conditions: 50 °C, p_{H_2} = 70 bar, p_{CO} = 5 bar, $[Co_2(CO)_8]$ = 0.115 M, toluene solution, reaction time 10 min. (The dash line shows the equilibrium value measured in the case of pyridine.)

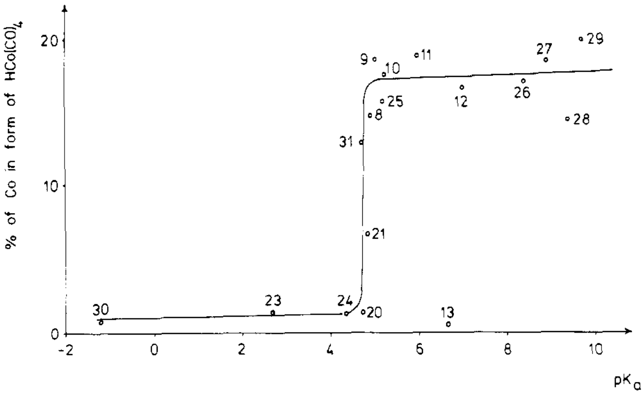

Figure 2. $HCo(CO)_4$ concentration as a function of the basicity of N heterocyclic or P bases (numbering and reaction conditions, see Table I). The pK_a values of the bases were taken or calculated from the literature.[11]

The accelerating effect of various pyridine derivatives, phosphines, and phosphites correlates characteristically with their basicity (Figure 2). Only the sterically strongly hindered 2,6-dimethylpyridine seems to behave excep-

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tionally (cf. ref 6). At the same time, the base/Co ratio leading to maximum $HCo(CO)_4$ concentration decreases with increasing basicity of the additives $P(OBu)_3$ < py < PBu_3 (Figure 1).

The nitrogen and phosphorus bases catalyzing the hydrogenation of $Co_2(CO)_8$ in our study disproportionate $Co_2(CO)_8$—if applied in stoichiometric amounts—to $[CoB_6][Co(CO)_4]_2$ and $[Co(CO)_nB_{5-n}][Co(CO)_4]$ where B is a N or P base and $n = 1, 2,$ or 3.[7] Halide ions were described to accelerate the disproportionation of cobalt carbonyls.[12] The mechanism of these reactions seems to be rather complex as suggested by some recent results.[13] More information about this disproportionation and about the hydrogenation of $Co_2(CO)_8$ itself is necessary to explain the mechanism of the catalytic effect reported in this work. Kinetic investigations, which are in progress, could contribute to clear some of the open questions.

Acknowledgment. We are grateful to L. Nêmeth for technical assistance.

Registry No. $Co_2(CO)_8$, 10210-68-1; pyridine, 110-86-1.

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Characterization of an Unusual Binuclear Rhodium Complex with Bridging 2-[Bis(diphenylphosphino)methyl]pyridine (PNP) Ligands

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Summary: An unusual bis(phosphine)-bridged binuclear complex in which the P atoms are arranged trans on one Rh and cis on the other has been synthesized by reaction of $[Rh(Cl)_2(CO)_2]^-$ with PNP ligand in ethanol in the presence of $NaBPh_4$. The single-crystal X-ray structure of $[Rh_2(CO)(\mu\text{-PNP})_2](BPh_4)_2$ has been determined.

Recently there has been considerable interest in the use of bridging bi- and polydentate phosphine and phosphine–pyridine ligands to hold two or more metals in close proximity.[1-6] We have recently reported that 2-[bis(diphenylphosphino)methyl]pyridine, $[Ph_2P]_2CHC_5H_5N$ = PNP, can function as a tridentate ligand to one metal, $[Rh(norbornadiene)(PNP)]PF_6$,[6] or as a bridging bis(phosphine) ligand which gives a binuclear complex of the face-to-face type with trans phosphorus atoms and with the pyridyl nitrogen atoms bound, $[Rh_2(CO)_2(\mu\text{-PNP})_2](PF_6)_2$ (**1**).[5] We now report on the synthesis and characterization of an unusual PNP-bridged binuclear complex of rhodium $[Rh_2(CO)(\mu\text{-PNP})_2](BPh_4)_2$ (**2**), in which the phosphorus atoms are arranged trans on one rhodium and cis on the other (vide infra). This trans,cis phosphorus stereochemistry is very rare among bis(phosphine)-bridged binuclear complexes and has been previously observed only in $[Pt_2(CH_3)_3(\mu\text{-dppm})_2](PF_6)$[7] and in the bis(phosphazane)-bridged complex $[Rh_2(CO)Cl_2\{\mu\text{-}(PhO)_2PN(Et)P(OPh)_2\}_2]$.[8] Therefore, complex **2** is the first structurally characterized example of a bis(phosphine)-bridged binuclear rhodium complex of a simple dppm-type ligand which contains this unusual stereochemistry.

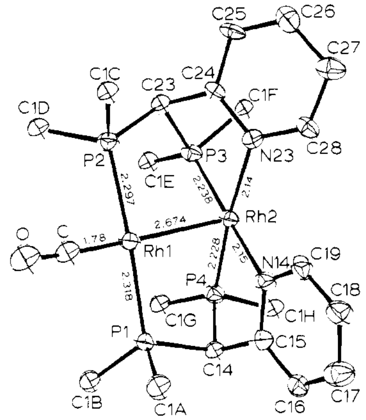
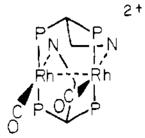
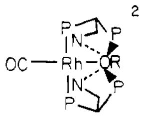


Figure 1. An ORTEP drawing of the dication of $[Rh_2(CO)(\mu\text{-PNP})_2](BPh_4)_2{\cdot}2CH_2Cl_2$. Phenyl carbon atoms have been omitted for clarity and are numbered C1A, C2A, ..., C_6A for rings A–H. Some selected bond angles and distances are Rh1–Rh2–P3 = 94.9 (1)°, Rh1–Rh2–P4 = 88.7 (1)°, Rh1–Rh2–N14 = 82.3 (3)°, Rh1–Rh2–N23, 97.9 (3)°, Rh2–Rh1–P1 = 92.3 (1)°, Rh2–Rh1–P2, 88.2 (1)°, Rh2–Rh1–C, 166.5 (5)°, P1–Rh1–C = 90.0 (5)°, P2–Rh1–C = 91.2 (5)°, Rh1–C–O, 176 (1)°, and C–O = 1.18 (1) Å.



1



2

The reaction of a stoichiometric amount of PNP ligand[6] dissolved in a minimal amount of CH_2Cl_2 with the lithium salt of $[Rh(CO)_2Cl_2]^{-}$[9] in ethanol saturated with CO resulted in the immediate formation of a red solution. The solution was purged with N_2 and stirred for several hours. A purple precipitate formed upon the addition of an ethanol solution of $NaBPh_4$ and red-orange crystals were obtained by recyrstallization of the precipitate from a CH_2Cl_2–C_2H_5OH solution. The purple color is due to the presence of **1** which is converted into **2** during the recrystallization process. All manipulations were carried out under a purified atmosphere of N_2. The yield of **2** was 70%.[10] ^{31}P NMR of the crude product shows that **2** is

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