matography (4:1 hexane–Et$_2$O) gave 72 mg (63%) of 2-(ethoxymethyl)-3-methyl-1,4-naphthoquinone: yellow solid; mp 61–62 °C (petroleum ether); IR (CH$_2$Cl) ν(CO) 1660 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.02 (m, 2 H), 7.63 (m, 2 H), 4.48 (s, 2 H), 3.55 (q, J = 7 Hz, 2 H), 2.25 (s, 3 H), 1.20 (t, J = 7 Hz, 3 H). Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.02; H, 6.13. Found: C, 72.81; H, 6.19.

2-(Diethoxymethyl)-3-methyl-1,4-naphthoquinone was prepared as described above from cobalt complex **6** (400 mg, 0.05 mmol), 1, 1-diethoxy-2-butyne (106 mg, 0.75 mmol), and 5 mL of CH$_2$Cl$_2$ for 2 h at 80 °C with the saturated NaHCO$_3$ wash in the workup. Medium-pressure chromatography (3:2 hexane–Et$_2$O) gave 2-(diethoxymethyl)-3-methyl-1,4-naphthoquinone (70 mg, 51%) as a yellow solid: mp 44–45 °C (cold petroleum ether); IR (CH$_2$Cl$_2$) ν(CO) 1660 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.00 (m, 2 H), 7.60 (m, 2 H), 5.88 (s, 1 H), 3.77 and 3.63 (overlapping quartets, J = 7 Hz, 4 H), 2.38 (s, 3 H), 1.23 (t, J = 7 Hz, 6 H). Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.05; H, 6.61. Found: C, 70.28; H, 6.75.

3-Ethyl-2-(2-(tetrahydropyranyloxy)ethyl)-1,4-naphthoquinone was prepared as described above from cobalt complex **6** (400 mg, 0.50 mmol), 1-hydroxy-3-hexynyl tetrahydropyranyl ether (101 mg, 0.60 mmol), and 5 mL of CH$_2$Cl$_2$ for 2 h at 80 °C with the saturated NaHCO$_3$ wash in the workup. Medium-pressure chromatography (3:2 hexane–Et$_2$O) gave 110 mg (73%) of 3-ethyl-2-(2-(tetrahydropyranyloxy)ethyl)-1,4-naphthoquinone as a yellow solid: mp 70.5–71 °C (petroleum ether); IR(CH$_2$Cl$_2$) ν(CO) 1655 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.97 (m, 2 H), 7.58 (m, 2 H), 4.57 (br s, 1 H), 3.67 (m, 4 H), 2.97 (t, J = 7 Hz, 2 H), 2.23 (s, 3 H), 1.60 (m, 6 H). Anal. Calcd for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71. Found: C, 71.85; H, 6.86.

na

Acknowledgment is made to the National Cancer Institute, D.H.E.W. (Grant CA 26374), for support of this work.

Registry No. **1**, 75895-97-5; **3**, 80907-49-9; **4**, 80907-51-3; **5**, 80907-53-5; **6**, 80907-55-7; **7**, 80925-49-1; CoCl(PPh$_3$)$_3$, 26305-75-9; benzocyclobutenedione, 6383-11-5; 2-*n*-butyl-1,4-naphthoquinone, 34491-88-8; 2,3-diethyl-1,4-naphthoquinone, 2397-59-3; 2-*n*-butyl-3-(trimethylsilyl)-1,4-naphthoquinone, 75909-64-7; 2-(ethoxymethyl)-3-methyl-1,4-naphthoquinone, 80906-68-9; 2-(diethoxymethyl)-3-methyl-1,4-naphthoquinone, 80906-69-0; 3-ethyl-2-(2-(tetrahydropyranyloxy)ethyl)1,4-naphthoquinonel, 80906-70-3; 1-hexyne, 693-02-7; 3-hexyne, 928-49-4; 1-(trimethylsilyl)-1-hexyne, 3844-94-8; ethyl 2-propynyl ether, 628-33-1; 1,1-diethoxy-2-butyne, 2806-97-5; 1-hydroxy-3-hexynyl tetrahydropyranyl ether, 70482-82-5; CoCl$_2$(PPh$_3$)$_2$, 14126-40-0.

Selective Phase Transfer and Palladium(0)-Catalyzed Carbonylation, Carbalkoxylation, and Reduction Reactions

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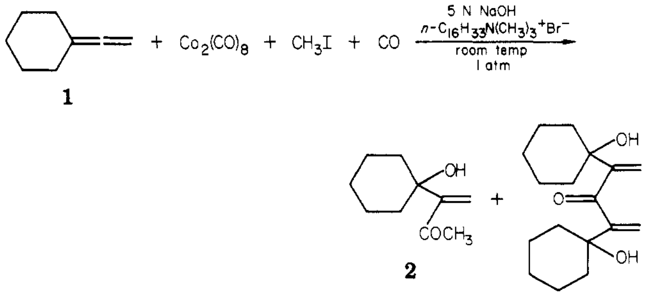
Tetrakis(triphenylphosphine)palladium can catalyze the carbonylation of benzylic halides to carboxylic acids using 5 N NaOH and CH$_2$Cl$_2$ at room temperature and 1 atm of pressure. Although the presence of tetrahexylammonium hydrogen sulfate (a phase-transfer catalyst) improves the product yield, it is not necessary to use a quaternary ammonium salt in these reactions. Reduction (and coupling) of halides occurs by using bis(dibenzylideneacetone)palladium as the catalyst under phase-transfer conditions (no reaction takes place in the absence of the phase-transfer catalyst). Esters were obtained by the phase transfer catalyzed carbonylation of halides in the presence of Pd(diphos)$_2$ [diphos = 1,2-bis(diphenylphosphino)ethane] while acids were the principal products formed in the absence of the quaternary ammonium salt.

During the past five years, there have been a considerable number of applications of phase-transfer catalysis to stoichiometric and catalytic organometallic reactions.[2] Of particular importance are reactions involving cobalt carbonyl as the organometallic species [e.g., **1** → **2** and **3**].[3]



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Few examples are known involving the use of palladium(0) compounds as catalysts in phase-transfer processes. The tetrakis(triphenylphosphine)palladium(0)-catalyzed cyanation of vinyl halides (**4** → **5**) can be attained in excellent yields using crown ether catalysis. However, quite drastic conditions are required.[4] The use of rather severe conditions [95 °C (5 atm)] has also been reported for the carbonylation of halides by palladium catalysts.[5] Although bis(triphenylphosphine)palladium dichloride (with added triphenylphosphine) was employed as the catalyst, Cassar and co-workers[5] assumed that tetrakis(triphenyl-

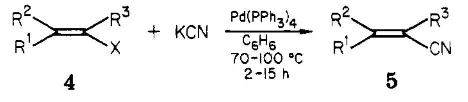

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Table I. Products Obtained from the Pd(0)-Catalyzed Carbonylation of 6

6				yield,[a] %			
Ar =; X =	PdL_n	$(C_6H_{13})_4N^+HSO_4^-$	organic phase	7	8	9	10
2-naphthyl; Br	$Pd(PPh_3)_4$	yes	CH_2Cl_2	63	4		1-2
	$Pd(PPh_3)_4$	yes	C_6H_6	84			
	$Pd(PPh_3)_4$	no	C_6H_6	73			
	$Pd(dba)_2$	yes	C_6H_6	2	66		
	$Pd(dba)_2$	yes	CH_2Cl_2[b]		56		15
	$Pd(dba)_2$	yes	CH_2Cl_2[c]		95		
	$Pd(diphos)_2$	yes	CH_2Cl_2	24			65
	$Pd(diphos)_2$	no	CH_2Cl_2[d]	85			8
Ph; Br	$Pd(PPh_3)_4$	yes	CH_2Cl_2	84			
	$Pd(PPh_3)_4$	no	CH_2Cl_2[e]	57			
	$Pd(dba)_2$	yes	C_6H_6			48	
p-$CH_3C_6H_4$; Br	$Pd(dba)_2$	yes	CH_2Cl_2			72	
	$Pd(dba)_2$	no	CH_2Cl_2[f]				
	$Pd(diphos)_2$	yes	CH_2Cl_2[e]				54
	$Pd(diphos)_2$	no	CH_2Cl_2	74		16	
o-$CH_3C_6H_4$; Br	$Pd(PPh_3)_4$	yes	CH_2Cl_2[g]	58	19		
	$Pd(dba)_2$	yes	CH_2Cl_2		32	42	
	$Pd(diphos)_2$	yes	CH_2Cl_2				84[h]
	$Pd(diphos)_2$	no	CH_2Cl_2	62			
o-$CH_3C_6H_4$; Cl	$Pd(dba)_2$	yes	CH_2Cl_2		50		
	$Pd(diphos)_2$	yes	CH_2Cl_2				75
	$Pd(diphos)_2$	no	CH_2Cl_2	72			
p-FC_6H_4; Br	$Pd(PPh_3)_4$	yes	CH_2Cl_2	79			
	$Pd(dba)_2$	yes	CH_2Cl_2		63		
	$Pd(diphos)_2$	yes	CH_2Cl_2[f]				

[a] Yields are of pure products. Products were identified by comparison of spectral data (IR, NMR, MS) with those of authentic materials. [b] 2-Naphthalenemethanol was also formed in 10% yield. [c] A 1:1 CO/H_2 atmosphere was used. [d] An unidentified byproduct was also formed with MS (*m/e* 354). It may be the α-keto ester related to **10**. [e] 40-42% starting material was recovered. [f] No reaction. [g] $(o\text{-}CH_3C_6H_4CH_2)_2CO$ was obtained in 12% yield. [h] New compound: IR $(CHCl_3)$ ν_{CO} 1735 cm^{-1}; ^1H NMR $(CDCl_3)$ δ 2.20 (s, 6 H, methyls), 3.53 (s, 2 H, CH_2CO), 5.02 (s, 2 H, OCH_2), 7.05 (br s, 8 H, aromatic protons); MS *m/e* 254 $[M]^+$. Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.22; H, 7.35.

phosphine)palladium(0) was the true catalytic species in these reactions (eq 1 of ref 5).

Some significant ligand effects were recently observed in the palladium(0)-catalyzed carbonylation of azirines to β-lactams or vinyl isocyanates (nonphase-transfer reactions).[6] It seemed of interest to learn whether the ligands, attached to the metal, would have any influence on a palladium complex catalyzed phase-transfer process. We now wish to report that the palladium(0)-catalyzed carbonylation of benzylic halides is very sensitive to the nature of the ligands attached to the metal, with the occurrence of selective carbonylation, carbalkoxylation, and dehalogenation.

Initially, we repeated the work by Cassar et al.[5] using tetrakis(triphenylphosphine)palladium(0) as the metal catalyst and tetrahexylammonium hydrogen sulfate as the phase-transfer agent and made several unexpected findings. First, the carbonylation in fact occurs under very mild conditions [room temperature (1 atm)]. Second, it is not necessary to add triphenylphosphine. Third, and most striking, is the observation that the carbonylation reaction is *not* an authentic phase-transfer process. If, for example, 2-(bromomethyl)naphthalene (**6**, Ar = 2-naphthyl, X = Br) is used as the organic substrate, the yield (Table I) of (2-naphthyl)acetic acid (**7**, Ar = 2-naphthyl) is nearly as high (73% vs. 84%) in the absence as in the presence of the phase-transfer catalyst. In addition, while phenyl acetic acid (**7**, Ar = Ph) was obtained from benzyl bromide in 57% yield in the absence of a phase-transfer catalyst, the presence of the quarternary ammonium salt afforded the product acid in 84% yield. The results demonstrate that this carbonylation reaction is a two-phase process which does not require a phase-transfer catalyst, although the presence of such a catalyst does improve the yield.

$$\underset{\mathbf{6}}{ArCH_2X} + CO \xrightarrow[\substack{CH_2Cl_2(\text{or } C_6H_6)\\ 5\text{ N NaOH}\\ (C_6H_{13})_4N^+HSO_4^-}]{PdL_n} \underset{\mathbf{7}}{ArCH_2COOH} +$$

$$\underset{\mathbf{8}}{ArCH_3} + \underset{\mathbf{9}}{ArCH_2CH_2Ar} + \underset{\mathbf{10}}{ArCH_2C({=}O)OCH_2Ar}$$

If one uses a palladium catalyst containing a bidentate acceptor ligand, bis(dibenzylideneacetone)palladium(0) [i.e., $Pd(dba)_2$], instead of the monodentate donor ligand, triphenylphosphine, then little or no carbonylation of **6** was observed but rather the dehalogenated hydrocarbons (**8**, **9**) were formed. This is a true phase-transfer reaction since starting material was recovered when the $Pd(dba)_2$-catalyzed carbonylation was effected in the absence of the phase-transfer agent. The isolation of **8** and **9** in these reactions is suggestive of the participation of free-radical intermediates in this phase-transfer process. Free radicals may be involved in the cobalt carbonyl catalyzed carbonylation of certain phase-transfer catalysts[7] and of halides by irradiation.[8] It should also be noted that the yields of reduced products can be increased substantially by using a syngas (i.e., 1:1 Co/H_2) instead of a carbon monoxide atmosphere for the $Pd(dba)_2$-catalyzed reactions.

The use as catalyst of $Pd(diphos)_2$ [where diphos = 1,2-bis(diphenylphosphino)ethane], which contains a bidentate donor ligand, results in a third and rather unusual reaction pathway—carbalkoxylation. The ester **10** was the major or only product obtained when **6**, Ar = 2-naphthyl, p-$CH_3C_6H_4$, and o-$CH_3C_6H_4$ and X = Br, and **6**, Ar = o-$CH_3C_6H_4$ and X = Cl, were used as the organic reactants.

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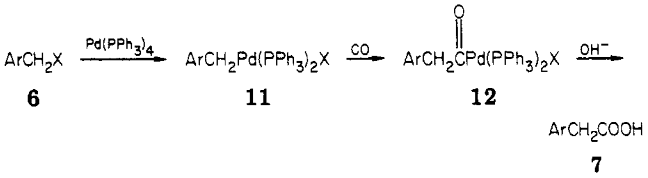
Scheme I



Remarkably, the carboxylic acid **7** was the major product obtained when the carbonylation reaction was run in the *absence* of the phase-transfer catalyst. In other words, $Pd(PPh_3)_4$ and $Pd(diphos)_2$ behave in a similar manner using biphasic but not phase-transfer conditions.

The mechanistic scheme given by Cassar and co-workers[5] for the tetrakis(triphenylphosphine)palladium(0)-catalyzed carbonylation of halides involves the alkyl- and acylpalladium complexes, **11** and **12**, respectively, as intermediates (Scheme I). The principal function of the two-phase medium is the hydroxide ion cleavage of **12** at the interface to give **7** which, once formed, is transferred to the aqueous phase. This scheme, while reasonable, cannot account for the results described herein.

An alternative pathway, which merits consideration, involves the participation of hydroxide ion in the initial stages of the process (Scheme II). Hydroxide ion displacement of one of the phosphine ligands of $Pd(PPh_3)_4$ would give **13**. For $Pd(dba)_2$ and $Pd(diphos)_2$, one of the bidentate ligands would become monodentate. Complex **13** can then react with halide to give **14** which on carbonylation (**15**) and hydroxide ion cleavage of the palladium–carbon bond (or reductive elimination from **15**) would afford the acid **7**.

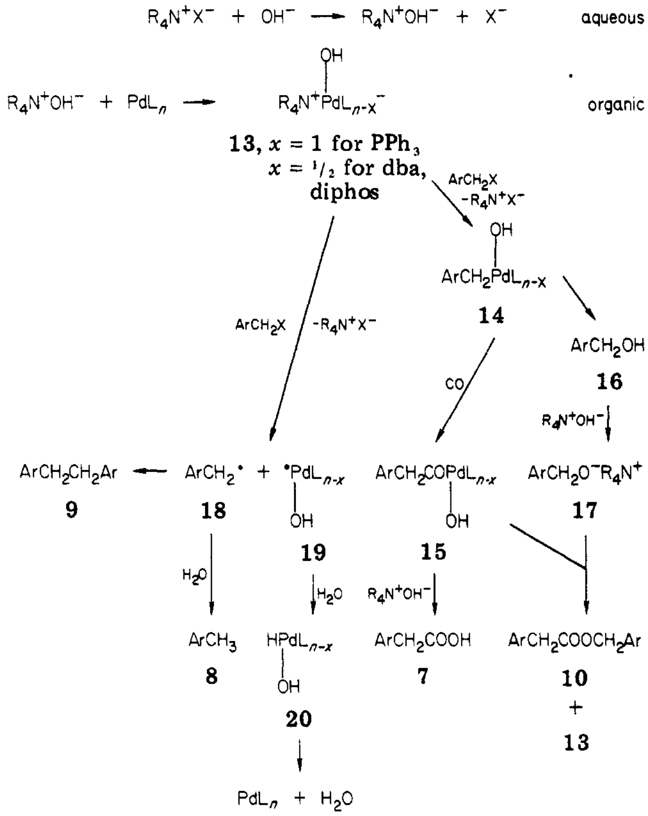
The ester **10** may result by reductive elimination of **14** to the benzylic alcohol (**16**), deprotonation to **17**, and reaction of the latter with **15** (**13** being regenerated as a byproduct). The difference in behavior of $Pd(PPh_3)_4$ and $Pd(diphos)_2$ may be a consequence of the ease of reductive elimination of **14** to **16**, with the conformationally more rigid bidentate diphos ligand facilitating the elimination process.

In addition to the ionic reaction of **13** with a halide, single electron transfer is also possible. It is conceivable that such a process would become important when an acceptor ligand such as dba is present. In that case, the benzylic radical **18** is formed along with the palladium radical **19**. Dimerization of **18** would afford the hydrocarbon **9**, while **8** would be formed on hydrogen abstraction from water. The latter process, applied to **19**, would give the palladium hydride (**20**) which, on reductive elimination of water, regenerates the palladium(0) catalyst.

How can one rationalize the different reaction pathways observed by using $Pd(diphos)_2$ as a catalyst under two-phase (acid) and phase-transfer catalysis (ester) conditions? With use of phase-transfer catalysis, the quaternary ammonium hydroxide in the organic phase deprotonates the benzylic alcohol (**16**), giving **17** which, as already noted, reacts with **15** to give the ester. In the two-phase process, however, any benzylic alcohol formed would migrate to the basic aqueous phase and the subsequently formed alkoxide anion (**17**) cannot compete with hydroxide ion for the acylpalladium intermediate (**15**).

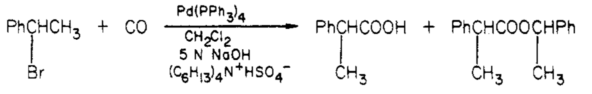
Could the benzylic alcohol **16** simply arise from hydroxide ion displacement of halide ion from the substrate (**6**)? When **6**, Ar = 2-naphthyl and X = Br, was reacted with carbon monoxide, aqueous sodium hydroxide, CH_2Cl_2, and the phase transfer agent [but no $Pd(diphos)_2$], the alcohol **16**, Ar = 2-naphthyl, was obtained in 15% yield with the remainder being recovered starting material.

Scheme II



Clearly, since **10** is formed in good yield, the $Pd(diphos)_2$ catalyst must participate in the formation of the alcohol **16**.

Finally, it was of interest to examine the palladium-catalyzed carbonylation of a secondary halide. When α-phenethyl bromide (**21**) was exposed to carbon monoxide by using $Pd(PPh_3)_4$ as the metal catalyst, 2-phenylpropionic acid (**22**) was obtained in 36% yield and the ester (**23**) was formed in 19% yield. The isolation of appreciable amounts of the ester may be a result of the greater effective bulk of the phenethyl group as compared to that of the benzyl group. This steric effect compensates for the previously noted difference between $Pd(diphos)_2$ and $Pd(PPh_3)_4$. Note that **21** is unreactive when $Pd(diphos)_2$ is used as the catalyst.



21 **22** **23**

$$PhCH(Br)CH_3 + CO \xrightarrow[\substack{CH_2Cl_2 \\ 5\ N\ NaOH \\ (C_6H_{13})_4N^+HSO_4^-}]{Pd(PPh_3)_4} PhCH(CH_3)COOH + PhCH(CH_3)COOCH(CH_3)Ph$$

In conclusion, the ligands attached to the metal have an important influence on the course of the palladium(0)-catalyzed carbonylation of benzylic halides using phase-transfer catalysis. Furthermore, the phase-transfer catalyst may [$Pd(dba)_2$, $Pd(diphos)_2$] or may not [$Pd(PPh_3)_4$] play a vital role in these reactions. A particularly novel feature of the $Pd(diphos)_2$ catalyzed reaction is the *change* in reaction pathway (carbonylation vs. carbalkoxylation) depending on whether one uses a phase-transfer catalyst.

Experimental Section

Elemental analyses were carried out by Canadian Microanalytical Service, Vancouver, Canada. Mass spectra were determined on an AEI MS902 spectrometer. Infrared spectral determinations were made with a Unicam SP-110 spectrometer, equipped with a calibration standard. Proton magnetic resonance spectra were recorded on Varian T60 and HA100 spectrometers, and carbon magnetic resonance spectral determinations were made in the fully and partially decoupled modes with a Varian FT-80 spectrometer.

Tetrakis(triphenylphosphine)palladium(0) was prepared following the procedure of Coulson,[9] and bis(dibenzylideneacetone)palladium(0)[10] and the Pd(diphos)$_2$ catalyst[11] were synthesized by using literature procedures. The organic reactants were commercial reagents. Solvents were dried and purified by standard methods.

General Procedure for the Palladium(0) and Phase Transfer Catalyzed Carbonylation of Halides. A mixture of tetrahexylammonium hydrogensulfate (0.11 mmol) in 5 N NaOH (15 mL) and the palladium catalyst [0.05 mmol, except Pd(dba)$_2$ where 0.20 mmol is used] in 15 mL of methylene chloride (or benzene) was stirred under a carbon monoxide atmosphere at room temperature. Then the halide (4.5–5.0 mmol) in methylene chloride (3–5 mL) was added, drop-by-drop, and after addition was complete, the reaction mixture was stirred for 6–10 h (followed by thin-layer chromatography). The layers were separated, and the acid **7** was obtained from the aqueous layer by acidification (pH 3) of the latter (followed by extraction if necessary). The organic layer was washed with water, dried (MgSO$_4$), and concentrated. Pure **8–10** were obtained by chromatography of the crude product(s) on silica gel.

Reactions effected in the absence of the phase-transfer agent or the palladium catalyst were run following the general procedure, except without the noted species. **23** is a new compound: ^{1}H NMR (CDCl$_3$) δ 1.50 (m, 6 H, methyls), 3.71 (q, 1 H, J = 7 Hz, PhCHCO), 5.83 (q, 1 H, J = 7 Hz, OCHPh), 7.10 (m, 10 H, aromatic protons); MS m/e 254 [M]$^+$. Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 79.69; H, 7.46.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council for support of this work.

Registry No. **6** (Ar = 2-naphthyl, X = Br), 939-26-4; **6** (Ar = Ph, X = Br), 100-39-0; **6** (Ar = p-$CH_3C_6H_4$, X = Br), 104-81-4; **6** (Ar = o-$CH_3C_6H_4$, X = Br), 89-92-9; **6** (Ar = o-$CH_3C_6H_4$, X = Cl), 552-45-4; **6** (Ar = p-FC_6H_4, X = Br), 459-46-1; **7** (Ar = 2-naphthyl), 581-96-4; **7** (Ar = Ph), 103-82-2; **7** (Ar = p-$CH_3C_6H_4$), 622-47-9; **7** (Ar = o-$CH_3C_6H_4$), 644-36-0; **7** (Ar = p-FC_6H_4), 405-50-5; **10** (Ar = 2-naphthyl), 53342-33-9; **10** (Ar = p-$CH_3C_6H_4$), 36707-18-3; **10** (Ar = o-$CH_3C_6H_4$), 80720-85-0; **21**, 585-71-7; **22**, 492-37-5; **23**, 80720-86-1; Pd(PPh$_3$)$_4$, 14221-01-3; Pd(dba)$_2$, 32005-36-0; Pd(diphos)$_2$, 31277-98-2.

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Reactivity of the Triethylphosphine–Carbon Disulfide Adduct toward Metal Carbonyls. X-ray Structures of the Complexes [Cr(CO)$_5$(S$_2$CPEt$_3$)] and [Mo(CO)$_2$(PEt$_3$)(μ-S$_2$CPEt$_3$)]$_2$

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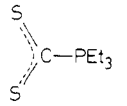
By reaction of the triethylphosphine–carbon disulfide adduct Et$_3$P·CS$_2$, Z, with group 6B metal carbonyls or isoelectronic iron and manganese carbonyl derivatives, the monomeric [M(CO)$_5$Z] (M = Cr, Mo, W), [Mn(η^5-C$_5$H$_5$)(CO)$_2$Z], and [Fe(η^5-C$_5$H$_5$)(CO)$_2$Z]BPh$_4$ and the dimeric [Mo(CO)$_2$(PEt$_3$)Z]$_2$ complexes have been prepared. The X-ray structure determinations of [Cr(CO)$_5$(S$_2$CPEt$_3$)] (1) and [Mo(CO)(PEt$_3$)(μ-S$_2$CPEt$_3$)]$_2$ (**6**) have been carried out from counter diffraction data. Crystal data for **1** are as follows: space group $P2_1/a$, a = 13.631 (7) Å, b = 12.311 (6) Å, c = 11.037 (6) Å, β = 100.76 (4) °, and Z = 4. Crystal data for **6** are as follows: space group $Pbca$, a = 14.132 (5) Å, b = 23.693 (9) Å, c = 12.667 (4) Å, and Z = 4. Both structures were solved by the heavy-atom method and refined by full-matrix least-squares techniques to R values of 0.057 and 0.056, respectively. The mononuclear complex **1** exhibits slightly distorted octahedral geometry with the Z molecule linked to the chromium atom by one sulfur atom as a two-electron σ donor. In the dimeric complex **6** each zwitterion coordinates to one metal through a η^3-S$_2$C-delocalized linkage as a four-electron pseudoallylic ligand and to the other metal through one sulfur atom as a two-electron σ donor. The coordination around each metal atom completed by two carbonyl groups and one phosphine may be considered pseudooctahedral. The mechanism for the formation of the dinuclear compound is proposed and discussed.

Introduction

The reactivity of the triethylphosphine–carbon disulfide adduct Et$_3$P·CS$_2$, Z, toward metal–ligand moieties formed by transition-metal cations and poly (tertiary phosphines) has been recently investigated in this laboratory. In particular, several mononuclear complexes have been described.[1,2] These complexes contain as ligands either Z coordinated to the metal via both sulfur atoms or different groups deriving from Z. The carbon atom of the CS$_2$ group, in fact, can be attacked by a variety of nucleophiles to give different disulfido ligands such as S$_2$CO^{2-}, S$_2$CS^{2-}, S$_2$CH$^-$, and S$_2$C(H)PEt$_3$$^-$. Furthermore, the P–CS$_2$ bond can be



Z

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