Synthesis of Halomethyl Complexes from Metal Formyls

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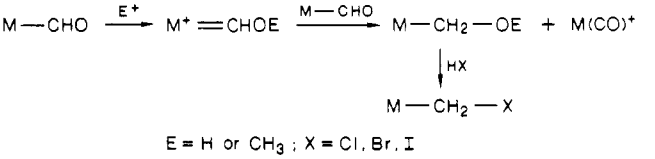
Summary: The ability of transition-metal formyl complexes to transfer hydride in the presence of electrophiles has been utilized in developing syntheses of halomethyl complexes (M-CH_2-X, M = Mo, Mn, Re; X = chlorine, bromine, iodine) from five neutral formyl complexes. In each case, the stereochemistry of the initial formyl complex is preserved in the halomethyl product.

Although the synthesis and chemistry of a number of metal-C_1 complexes have received a great deal of attention in recent years because of the importance of such compounds as models for catalytic intermediates,[1] one potentially very useful series, the monohalomethyl complexes, has been little studied. Currently, there are two principal synthetic routes to the halomethyl complexes. One of these involves nucleophilic displacement by a metal anion on a dihaloalkane or a holomethyl ether[2] (the latter procedure must be followed, usually, by HX cleavage of the resulting alkoxy methyl complex) and is, therefore, limited by the need for a nucleophilic anion. The second method involves, and is limited by, the need for oxidative addition of a dihalomethane to a coordinatively unsaturated metal complex.[3] Other, presently less general, routes have also been reported. Roper has prepared an osmium complex by HX cleavage of an η^2-formaldehyde complex and another by addition of chlorine to a carbene complex.[4] McCrindle[5] and Hubbard[6] have shown that direct reactions between diazomethane and some metal halides can provide good yields of the corresponding halomethyl complexes. Palyi[7] has successfully decarbonylated a (chloroacetyl)-cobalt complex, and Wieghardt[8] has prepared an iodomethyl complex by direct halogenation of the corresponding methyl complex. The limitations in the current methods and the belief that halomethyl complexes could play more important roles in organometallic synthesis have led us to explore alternative methods for their preparation.

Table I. Halomethyl Complexes and Formyl Precursors

formyl complex	halomethyl complex (yield)
trans-$CpMo(CO)_2[P(OPh)_3]CHO$	*trans*-$CpMo(CO)_2[P(OPh)_3]CH_2X$
	1a, X = Cl (75%)
	1b, X = Br (74%)
	1c, X = I (46%)
mer,trans-$Re(CO)_3[P(OPh)_3]_2CHO$	*mer,trans*-$Re(CO)_3[P(OPh)_3]_2CH_2X$
	2a, X = Cl (80%)
	2b, X = Br (74%)
	2c, X = I (84%)
cis-$Mn(CO)_4(PPh_3)CHO$	*cis*-$Mn(CO)_4(PPh_3)CH_2X$
	3a, X = Cl (78%)
	3b, X = Br (58%)
	3c, X = I (60%)
mer,trans-$Mn(CO)_3(PPh_3)_2CHO$	*mer,trans*-$Mn(CO)_3(PPh_3)_2CH_2X$
	4a, X = Cl (76%)
	4b, X = Br (81%)
	4c, X = I (78%)
mer,trans-$Mn(CO)_3[P(OPh)_3]_2CHO$	*mer,trans*-$Mn(CO)_3[P(OPh)_3]_2CH_2X$
	5a, X = Cl (65%)
	5b, X = Br (72%)
	5c, X = I (67%)

As part of our general efforts to increase the synthetic applications of metal formyl complexes,[9] we have established two additional routes to halomethyl complexes by taking advantage of the ability of some formyls to transfer hydride in the presence of electrophilic reagents. Fifteen halomethyl complexes have been prepared by these routes, only one of these (**3a**[2g]) has been reported previously. The generalized reaction scheme is illustrated below:



The halomethyl compounds and their formyl precursors are identified in Table I; the syntheses and characterization of the formyl complexes have been described by us previously.[9] In the preparation of compounds **1-3**, direct conversion of the formyl complex to the halomethyl complex occurs by the action of HX. With **4** and **5**, methyl triflate was the initial electrophile and synthesis (and isolation) of the methoxymethyl complex[10,11] was followed

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Table II. Spectroscopic Characterization of Halomethyl Complexes

compd	ν_{CO}, cm^{-1}	^{1}H NMR,[a] δ	^{13}C NMR,[a,b] δ
1a	1974 (s), 1897 (vs)[c]	7.35 (m), 4.78 (d, J_{PH} = 1.1 Hz), 4.24 (d, J_{PH} = 4.2 Hz)[d]	232.93 (d, J_{PC} = 36.0 Hz), 33.09 (d, J_{PC} = 14.3 Hz)[d]
1b	1955 (s), 1867 (vs, br)	7.35 (m), 4.81 (s), 4.01 (d, J_{PH} = 4.3 Hz)[d]	232.93 (d, J_{PC} = 35.9 Hz), 25.08 (d, J_{PC} = 14.1 Hz)[d]
1c	1965 (s), 1885 (vs)	7.34 (m), 4.78 (s), 3.17 (d, J_{PH} = 4.3 Hz)[d]	233.23 (d, J_{PC} = 36.0 Hz), −6.47 (d, J_{PC} = 13.9 Hz)[d]
2a	2070 (w), 1970 (s), 1933 (m)	7.25 (m), 3.73 (t, J_{PH} = 8.6 Hz)	190.03 (t, J_{PC} = 13.9 Hz), 187.65 (t, J_{PC} = 9.2 Hz), 16.75 (t, J_{PC} = 11.9 Hz)
2b	2070 (w), 1975 (s), 1935 (m)	7.26 (m), 3.43 (t, J_{PH} = 9.0 Hz)[d]	189.4 (t, J_{PC} = 13.8 Hz), 187.01 (t, J_{PC} = 9.1 Hz), 5.40 (t, J_{PC} = 12.3 Hz)[d]
2c	2070 (w), 1975 (s), 1935 (m)	7.26 (m), 2.57 (t, J_{PH} = 9.5 Hz)[d]	190.94 (t, J_{PC} = 13.9 Hz), 186.54 (t, J_{PC} = 8.7 Hz), −29.80 (t, J_{PC} = 12.5 Hz)[d]
3a	2070 (m), 2000 (s), 1976 (vs), 1945 (s)	7.66 (m), 3.23 (d, J_{PH} = 6.6 Hz)[e]	216.74 (d, J_{PC} = 12.7 Hz), 216.68 (d, J_{PC} = 20.7 Hz), 214.68 (d, J_{PC} = 20.6 Hz), 36.87 (d, J_{PC} = 14.3 Hz)[e]
3b	2068 (m), 2000 (s), 1976 (vs), 1945 (s)	7.66 (m), 3.15 (d, J_{PH} = 7.6 Hz)[e]	216.90 (d, J_{PC} = 15.4 Hz), 216.66 (d, J_{PC} = 21.8 Hz), 214.37 (d, J_{PC} = 15.6 Hz), 26.67 (d, J_{PC} = 12.7 Hz)[e]
3c	2066 (m), 1990 (sh), 1972 (vs), 1942 (s)	7.60 (m), 2.10 (d, J_{PH} = 8.1 Hz)[e]	217.84 (d, J_{PC} = 11.3 Hz), 217.16 (d, J_{PC} = 22.5 Hz), 214.25 (d, J_{PC} = 17.6 Hz), −6.49 (d, J_{PC} = 13.7 Hz)[e]
4a	2015 (w), 1925 (s), 1890 (m)	7.08 (m), 3.01 (t, J_{PH} = 8.3 Hz)	222.43 (t, J_{PC} = 21.2 Hz), 217.21 (t, J_{PC} = 17.5 Hz), 46.69 (t, J_{PC} = 13.0 Hz)
4b	2018 (w), 1927 (s), 1891 (m)	7.50 (m), 2.76 (t, J_{PH} = 9.0 Hz)	222.22 (t, J_{PC} = 20.6 Hz), 221.14 (t, J_{PC} = 17.7 Hz), 41.30 (t, J_{PC} = 13.4 Hz)
4c	2020 (w), 1930 (s), 1893 (m)	7.63 (m), 1.85 (t, J_{PH} = 9.0 Hz)	223.11 (t, J_{PC} = 21.1 Hz), 220.94 (t, J_{PC} = 20.8 Hz), 14.04 (t, J_{PC} = 11.7 Hz)
5a	2050 (vw), 1965 (vs), 1935 (s)	7.25 (m), 3.78 (t, J_{PH} = 9.5 Hz)[g]	215.55 (t, J_{PC} = 31.6 Hz), 214.30 (t, J_{PC} = 24.0 Hz), 36.70 (t, J_{PC} = 23.8 Hz)[g]
5b	2050 (vw), 1970 (vs), 1935 (m)[h]	7.27 (m), 3.46 (t, J_{PH} = 10.0 Hz)[e]	216.20 (t, J_{PC} = 32.4 Hz), 214.70 (t, J_{PC} = 24.5 Hz), 26.7 (t, J_{PC} = 25.1 Hz)[i]
5c	2040 (vw), 1960 (vs), 1930 (m)	7.01 (m), 3.00 (t, J_{PH} = 10.4 Hz)[i]	217.38 (t, J_{PC} = 32.9 Hz), 214.87 (br s), −5.47 (t, J_{PC} = 25.1 Hz)[i]

[a] Spectra recorded at 20 °C in CD_2Cl_2, except as noted. [b] Proton decoupled; CO and M–CH_2–X only. [c] Spectra recorded at room temperature show a small amount of the cis isomer; this is evidenced by a medium intensity shoulder at 1910 cm^{-1}. [d] At −10 °C. [e] At 20 °C in acetone-d_6. [f] At 20 °C in benzene-d_6. [g] At 0 °C, in CD_2Cl_2. [h] Upon standing, solutions of **5b** develop a band at 1990 cm^{-1} due to a decomposition product. [i] At 20 °C in toluene-d_8.

by reaction with HX. In all cases, the stereochemistry of the initial formyl complex was preserved in the halomethyl products. The spectral properties of compounds **1–5** are shown in Table II.[12] Product yields in Table I are based on reaction stoichiometry, but, as the equation indicates, 2 mol of formyl complex yield only 1 mol of halomethyl complex by this procedure. However, the metal carbonyl cation product (isolated in high yield from all reactions) is the precursor to the formyl complex in each case and can be recovered and recycled to improve the synthesis.

Reactions of the hydrogen halides with the formyl or methoxymethyl complexes were conducted at 0 °C by bubbling gaseous HCl or HBr into a solution of the substrate for a short time (about 1 min for reactions involving 1 mmol of substrate) or by addition of a stoichiometric amount of aqueous HI to the solution; after HX addition, the mixtures were allowed to warm to room temperature and reactions were complete within an hour. For the preparations of compounds **1**, **2**, and **3**, the reaction solvent was CH_2Cl_2. The presence of several equivalents (5–6) of benzyltriethylammonium halide in reactions leading to **2a** and **2b** was needed to suppress formation of the metallacycle generated by a competing cyclometalation reaction.[9a] The lability of some others required the use of less polar solvents (toluene for **4a–c** and ether for **5a,b**) to suppress side reactions. The metal carbonyl cation could be easily separated from the desired product in all cases because of its insolubility in nonpolar solvents.

Although $Re(CO)_3[P(OPh)_3]_2CHO$ was rapidly converted to the halomethyl complexes by the action of any hydrogen halide, we have not yet been able to transform the corresponding manganese complex similarly. Reactions of the manganese formyl complex with hydrogen halides appeared to convert it, completely, to the corresponding hydroxymethylidene cations.[13] Either the formyl group in the rhenium complex is not as basic as the one in the manganese analogue (so that free formyl complex is available to transfer hydride as required by the synthesis) or the rhenium complex is a kinetically better hydride donor.

Work is in progress to establish the further applicability of these techniques to the synthesis of halomethyl complexes.

(11) The precursor of **5a–c**, *mer,trans*-$Mn(CO)_3[P(OPh)_3]_2CH_2OCH_3$, was prepared as follows: *mer,trans*-$Mn(CO)_3[P(OPh)_3]_2CHO$ (1.0 g, 1.3 mmol) was dissolved in 15 mL of CH_2Cl_2 at 0 °C with stirring; to this was added a solution containing $CF_3SO_3CH_3$ (0.09 mL, 0.8 mmol) dropwise during 2 h. After an additional hour at 0 °C, the mixture was warmed to room temperature and solvent removed under vacuum. The residue was triturated with ether and the ether-soluble material separated, evaporated to dryness, and recrystallized from CH_2Cl_2/pentane to afford 0.4 g (80%) of the methoxymethyl complex. The ether-insoluble residue was recrystallized from CH_2Cl_2 to afford *trans*-$Mn(CO)_4[P(OPh)_3]_2^+$-$CF_3SO_3^-$, 0.5 g (92%). The bis(phosphine) methoxy complex was prepared similarly. Anal. Calcd for $C_{41}H_{35}O_{10}P_2Mn$: C, 61.20; H, 4.38; P, 7.70. Found: C, 60.87; H, 4.50; P, 7.56. IR (CH_2Cl_2): ν_{CO} 2040 (vw), 1958 (vs), 1935 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.24 (m), 4.01 (t, J_{PH} = 8.1 Hz), 3.16 (s). ^{13}C NMR (CD_2Cl_2): δ 217.95 (t, J_{PC} = 33.3 Hz), 215.52 (t, J_{PC} = 21.0 Hz), 152.00 (t, J_{PC} = 5.1 Hz), 129.89 (s), 125.05 (s), 121.44 (s), 68.49 (t, J_{PC} = 20.8 Hz), 64.09 (s).

(12) Microanalytical data have been obtained on ten of the halomethyl compounds. Anal. Calcd for **1a** (Found): C, 54.14 (54.05); H, 3.84 (3.72); P, 5.37 (5.02). Calcd for **1b** (Found): C, 50.26 (50.34); H, 3.57 (3.69); Br, 12.86 (13.03). Calcd for **2a** (Found): C, 51.09 (51.11); H, 3.43 (3.44); Cl, 3.77 (3.67). Calcd for **2b** (Found): C, 48.79 (48.94); H, 3.28 (3.20); Br, 8.11 (8.13). Calcd for **2c** (Found): C, 46.57 (46.70); H, 3.13 (3.09); I, 12.30 (12.21). Calcd for **3b** (Found): C, 52.80 (52.40); H, 3.28 (3.40). Calcd for **3c** (Found): C, 48.45 (48.60); H, 3.01 (3.09). Calcd for **4a** (Found): C, 67.38 (67.47); H, 4.52 (4.66); P, 8.69 (8.70). Calcd for **4b** (Found): C, 63.43 (62.80); H, 4.26 (4.35); Br, 10.55 (10.23). Calcd for **5b** (Found): C, 56.29 (56.61); H, 3.78 (3.86); Br, 9.36 (9.24). Analyses were performed by Galbraith Laboratories, Knoxville, TN. The other halomethyl complexes have been characterized by spectral means (see Table II).

(13) The spectral properties of these products are similar to the hydroxymethylidene cations prepared from $Mn(CO)_3(PPh_3)_2CHO$.[9a]

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Isolation of a Bis(η^4-arene)dipalladium(I) Complex during the Annelation of Palladated Aryl Groups with Diphenylacetylene[1]

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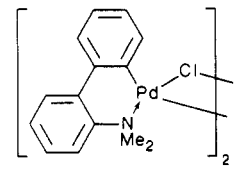
Summary: The palladated aryl units obtained via cyclopalladation of methyl 2-biphenylyl sulfide or *N*,*N*-dimethyl-2-biphenylamine undergo annelation reactions with diphenylacetylene. From the reaction of the sulfur containing palladocycle with the alkyne, an organometallic intermediate has been isolated in which two arene moieties are η^4-coordinated to a dipalladium(I) unit.

In the final stage of palladium-mediated stoichiometric or catalytic reactions in organic synthesis, the metal is usually recovered as palladium(II) or palladium(0) through reductive elimination reactions during which the metal is reduced by two-electron processes.[2] We wish here to report a rare example of such a reaction in which the metal is found as a palladium(I) complex together with the functionalized organic substrate.

We have shown earlier that the reactions between cyclopalladated compounds and internal alkynes can afford selectively heterocyclic compounds.[3] While investigating the potentiality of this reaction for the purpose of organic synthesis, we became interested in the behavior of such compounds in which the palladium atom is part of six-membered rings.[4] The new compounds **1** and **2** have thus been synthesized in almost quantitative yields through classical palladation[5] of the corresponding ligands using palladium acetate as the metalating agent followed by metathesis of the acetato groups with lithium chloride. The chloride-bridged dimer **1** was converted in situ into the cationic species **3** by abstracting the chloride ion with



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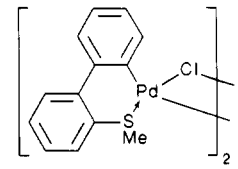

2

$AgSO_3CF_3$ in a THF solution. After removal of AgCl and the solvent, the residue thus obtained was treated in CH_2Cl_2 with excess of diphenylacetylene (PhC≡CPh:**3** > 4) to afford after 5 min of stirring at room temperature a brown solution from which compound **5** was quantitatively precipitated by addition of *n*-pentane (see Scheme I). Analytical data indicated that two alkyne units have been incorporated per palladium atom. The ^1H NMR spectrum of **5** displayed moreover characteristic resonance patterns for the four protons of the cyclohexadienyl unit η^3-bonded to Pd.[6] A related spirocyclic organopalladium compound has been fully characterized recently in our laboratory.[4] The molecule of water in **5** (detected by NMR, IR, and microanalysis) comes most probably from the silver triflate used, a feature that has already been observed in similar cationic compounds.[4]

When the cationic compound **4** (synthesized through addition of $AgBF_4$ to **2** in a CH_2Cl_2/MeCN solution[3]) was heated with a slight excess of diphenylacetylene (PhC≡CPh:**4** = 2.1) in chlorobenzene at 90 °C, it afforded a red solution after ca. 10 min. Filtration of this solution through a Celite column, removal of the chlorobenzene under reduced pressure, and washing the solid thus obtained with pentane afforded deep red **6** in 86% yield. The ^1H NMR spectrum of this compound did not allow the detection of any other organometallic species; thus the formation of **6** was indeed quantitative. The molecular structure of this compound was ascertained by an X-ray diffraction study[7] since its NMR spectra were of little help in order to determine its geometry. Crystals of **6** suitable for the X-ray analysis (which contain four molecules of acetone of crystallization) were obtained from an acetone/diethyl ether solution. The cationic part of the molecule is shown in Figure 1. It reveals that the former palladated aryl ring in **4** has been annelated by two diphenylacetylene reagents to form a pentasubstituted naphthalene derivative.[8] Two aryl rings of this latter ligand are both η^4-coordinated to a dipalladium unit. This gives rise to a so-called sandwich

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(5) See, for example: Hiraki, K.; Fuchita, Y.; Takechi, K. *Inorg. Chem.* **1981**, *20*, 4316.

(6) All new compounds gave satisfactory elemental analyses. Selected spectroscopic data are as follows: ^1H NMR ($CDCl_3$, 293 K, 200.13 MHz): **5**, δ 8.62–6.31 (m, 24 H, aromatic), 6.13 (d, 1 H, H^1), 6.01 (dd, 1 H, H^3, ^3J (H^2H^3) = 5.7 Hz), 5.57 (d, 1 H, H^4, ^3J (H^3H^4) = 8.0 Hz), 4.80 (t, 1 H, H^2, ^3J (H^1H^2) = 6.1 Hz), 2.78 and 1.49 (2s, 6 H, NMe_2), 1.75 (s, 2 H, H_2O) (H^1–H^4 represent the protons of the hexadienyl unit in **5**); **6**, δ 7.80–5.52 (28 H, aromatic), 2.29 (s, 3 H, SMe); **7**, δ 7.62–6.58 (m, 28 H, aromatic + NH), 2.29 (s, 6 H, NMe_2); **8**, δ 7.71–6.60 (m, 27 H, aromatic), 2.24 (s, 3 H, SMe). IR (KBr pellets): **7**, 3040 cm^{-1} (ν(NH)). MS (FAB): **7**, *m*/*z* 553 (552, $M^+ - H$); **8**, *m*/*z* 554 (554, M^+), 539 (M – Me), 507 (M – SMe).
(7) Crystal structure of **6** $((CH_3)_2CO)_4$: triclinic; space group $P\bar{1}$; a = 15.776 (6) Å, b = 19.786 (6) Å, c = 15.486 (6) Å, α = 91.79 (2)°, β = 114.88 (2)°, γ = 106.79 (2)°; V = 4132 Å^3, Z = 2; ρ_{calcd} = 1.234 g cm^{-3}; F_{000} = 1564; λ = 1.5418 Å; μ = 45.446 cm^{-1}; 8199 independent $\pm hkl$ reflections measured (Philips PW 1100/16 diffractometer, graphite-monochromated radiation, $\theta/2\theta$ flying step scan, 3° < θ < 50° at −100 °C). The structure was solved by using Patterson and Fourier methods and refined by full-matrix least squares by using 6918 observed reflections ($I > 3\sigma(I)$). Hydrogen atoms were introduced in structure factor calculations at their computed coordinates (C–H = 0.95 Å, B(H) = 1.3B_{eqv} (C)) but not refined. The fluorine atoms of one of the BF_4^- moieties are disordered over two positions in the ratio 1/1 (difference Fourier relative peak heights). Empirical absorption corrections were applied. $R(F)$ = 0.067; $R_w(F)$ = 0.110. Further details of the structure investigation can be obtained from the authors.
(8) (a) Dupont, J.; Pfeffer, M.; Daran, J. C.; Gauteron, J. *J. Chem. Soc., Dalton Trans.* **1988**, 2421. (b) Wee, G.; Rheingold, A. L.; Geib, S. J.; Heck, R. F. *Organometallics* **1987**, *6*, 1941.

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