The Preparation of Heterometallic Mo–Hg and Mo–Cu Complexes

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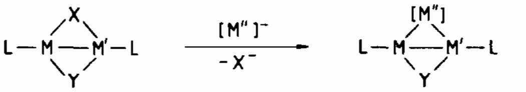
Abstract

The reaction of mercury(II) acetate with Na[$C_5H_5Mo(CO)_3$] in benzene gives the dinuclear compound $C_5H_5Mo(CO)_3Hg(\eta^2\text{-}O_2CCH_3)$ (3) which in solution is slowly converted to $Hg[C_5H_5Mo(CO)_3]_2$ (4) and $Hg(OAc)_2$. The complex $C_5H_5Mo(CO)_3HgSBu^t$ (6) is prepared from $(\mu\text{-}SBu^t)_2Hg_2(OAc)_2L_2$ (5) and $Na[C_5H_5Mo(CO)_3]$. Treatment of $(C_5H_5)_2Mo(SBu^t)_2$ (7) with $[(PMe_3)CuCl]_4$ gives a mixture of products from which $[(C_5H_5)_2Mo(\mu\text{-}SBu^t)_2CuCl]_2$ (9) and $(C_5H_5)_2MoCl(SBu^t)$ (11) have been isolated. The heterometallic dinuclear compounds $[(C_5H_5)_2Mo(\mu\text{-}SPh)_2Cu(PPh_3)_2]BF_4$ (12) and $(C_5H_5)_2Mo(\mu\text{-}SBu^t)_2\text{-}CuSBu^t$ (13) are prepared from $(C_5H_5)_2Mo(SPh)_2$, $[Cu(CH_3CN)_4]BF_4$ and PPh_3, and from 7 and $CuSBu^t$, respectively. The synthesis of $(C_5H_5)_2Mo(OAc)_2$ (14) and $[(C_5H_5)_2Mo(\eta^2\text{-}O_2CCH_3)]PF_6$ (15) is also described.

Introduction

Following the discovery that dinuclear Pd–Pd, Pt–Pt, and Pd–Pt complexes of general composition $(\mu\text{-}X)(\mu\text{-}Y)M_2(PR_3)_2$, where Y is C_5H_5 or 2-RC_3H_4 and X a carboxylate or halide ligand, are useful starting materials for the synthesis of mixed-metal clusters (see eqn. (1)) [1–3] we tried to expand this new preparative method by using analogous systems having, in particular, acetate anions in a bridging position.



(1)

(M = M' = Pd, Pt; M = Pd; M' = Pt; L = PR_3 etc.)
([M'']$^-$ = [$Co(CO)_4$]$^-$, [$V(CO)_6$]$^-$, [$M(CO)_3C_5H_5$]$^-$ (M = Cr, Mo, W); Y = C_5H_5, 2-RC_3H_4 etc.)

One of the starting materials which we tried for this purpose were the pyridine adducts of copper(II) acetate 1 which according to X-ray structural analyses contain a similar L–M–M–L unit as found in the above-mentioned $(\mu\text{-}X)(\mu\text{-}Y)M_2(PR_3)_2$ complexes [4]. Instead of obtaining Cu_2M or Cu_2M_n clusters formed by stepwise displacement of the carboxylate groups by the [$C_5H_5M(CO)_3$]$^-$ nucleophile we isolated the heterometallic dinuclear compounds 2 in good yield (Scheme 1) [5]. Mechanistic studies revealed that the mononuclear acetato complexes $C_5H_5M(CO)_3OAc$ were intermediates in the formation of 2 which could be confirmed by independent

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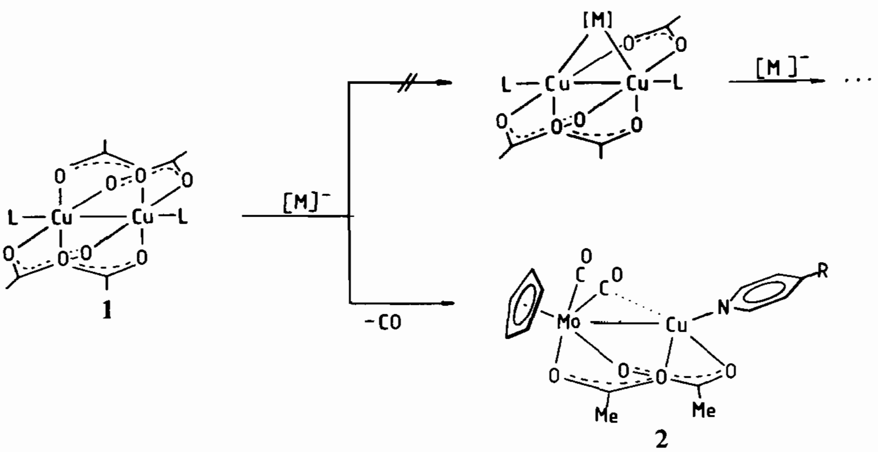


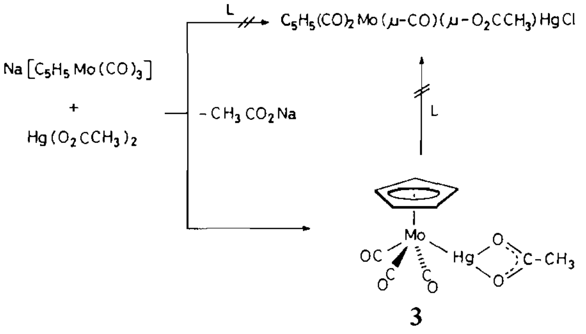
Scheme 1. (L = 4-RC_5H_4N, R = H, Me, Bu^t; [M] = $C_5H_5(CO)_3M$, M = Cr, Mo, W)

synthesis of 2 (M = Mo, W; R = CH_3) from $C_5H_5M(CO)_3OAc$, copper(I) acetate and 4-methylpyridine [5].

As a continuation of these studies we were interested to find out whether $Hg(OAc)_2$ can similarly be used as starting material for the preparation of heterometallic complexes with one or two acetate bridges and also, whether other types of dinuclear Mo–Cu compounds, similar or different in structure to 2, are accessible on a comparatively simple route. It is worth mentioning that a variety of Mo–Cu complexes are already known and that some of them are of biological significance, e.g. in the copper–molybdenum antagonism [6].

Results

Treatment of mercury(II) acetate with $Na[C_5H_5Mo(CO)_3]$ in benzene gives the dinuclear complex 3 in 56% yield (Scheme 2). The same product is formed also in presence of 4-methylpyridine. In contrast to the reaction of $Na[C_5H_5Mo(CO)_3]$ with 1 no reduction of the divalent metal occurs and by concomitant displacement of one CO group no acetate-bridged species is produced. 3 forms bright yellow, moderately air-stable crystals which are easily soluble in CH_2Cl_2 and aromatic hydrocarbons.



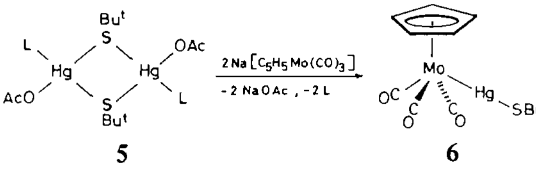
Scheme 2. L = 4-methylpyridine.

If a benzene solution of 3 is kept for several hours at room temperature, a new Mo–Hg compound is formed which by comparison with IR and NMR spectroscopic data reported in the literature [7] has been identified as $Hg[C_5H_5Mo(CO)_3]_2$ (4) (eqn. (2)). Complex 4 was first prepared by Fischer *et al.* [8] from $Hg(CN)_2$ and $Na[C_5H_5Mo(CO)_3]$ and subsequently characterized by X-ray analysis [9]. A similar equilibrium as shown in eqn. (2) has been observed by Mays and Robb [10] in the case of the analogous heterometallic compound $C_5H_5Mo(CO)_3HgCl$.

$$3 \rightleftharpoons \underset{4}{Hg[C_5H_5Mo(CO)_3]_2} + Hg(OAc)_2) \qquad (2)$$

The structural proposal for 3 (see Scheme 2) is mainly supported by the IR spectrum. The CO_2 stretching frequencies observed at 1580 and 1420 cm^{-1} are very reminiscent of bidentate acetate ligands [11] and thus 3 can well be compared with the compound $C_5H_5Mo(CO)_3HgS_2CNEt_2$ in which the dithiocarbamate is linked to the metal in a chelating mode [12]. We failed to prepare an acetate-bridged heterometallic complex of composition $C_5H_5(CO)_2Mo(\mu\text{-}OAc)(\mu\text{-}dppm)Hg$ by treatment of 3 with $CH_2(PPh_2)_2$ (dppm).

Besides $Hg(OAc)_2$, the dinuclear derivative $(\mu\text{-}SBu^t)_2Hg_2(OAc)_2L_2$ (5; L = 4-methylpyridine) which is obtained *in situ* from $[Hg(OAc)(SBu^t)]_n$ and L [13] has also been used as starting material for the synthesis of a Mo–Hg complex. Treatment of 5 with a twofold excess of $Na[C_5H_5Mo(CO)_3]$ in benzene leads to cleavage of the thiolate bridges and formation of $C_5H_5Mo(CO)_3HgSBu^t$ (6) (see eqn. (3)). Even under mild conditions the expected product $(\mu\text{-}SBu^t)_2\{Hg[Mo(CO)_3C_5H_5]L\}_2$ could not be observed which is presumably due to the weak Hg–L bonds and the high stability of $C_5H_5Mo(CO)_3HgX$ species.

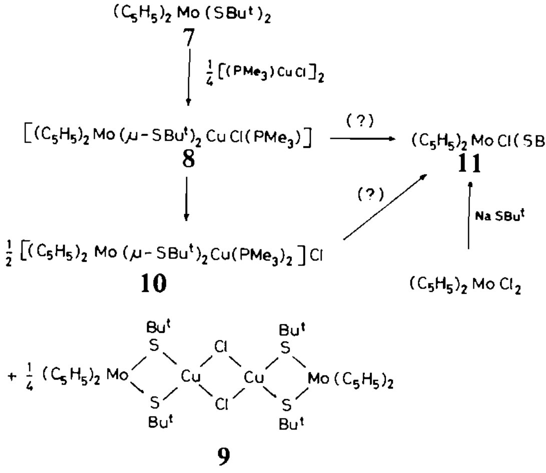


(3)

Various attempts to obtain trinuclear heterometallic compounds of the as yet unknown type $C_5H_5(CO)_3MoHg(\mu\text{-}OAc)(\mu\text{-}X)CuL_n$ (X = OAc or SBu^t) by reaction of 3 or 6 with copper(I) acetate in the presence of 4-methylpyridine remained unsuccessful. In all cases, formation of $L_2Cu_2(\mu\text{-}OAc)_4$ (1) occurred which was accompanied by precipitation of metallic mercury. In addition, side products such as $[C_5H_5Mo(CO)_3]_2$ (4) and (from 6 as the starting material) $[C_5H_5(CO)_2Mo]_2(\mu\text{-}SBu^t)_2$ [14] were obtained. It may be conceivable that at least in the reaction of 3 with CuOAc and L the expected trinuclear complex is formed as an intermediate which decomposes by heterometallic cleavage to give $C_5H_5Mo(CO)_3$ (stabilized as the dimer), Hg and 1.

The synthesis of new types of dinuclear Mo–Cu complexes having thiolate or acetate ligands in the bridging position was attempted by using derivatives of the well known dichloro compound $(C_5H_5)_2MoCl_2$ [15] as starting material. The bis(thiolato) complex $(C_5H_5)_2Mo(SBu^t)_2$ (7) already employed in our laboratory for the preparation of mixed-metal Mo–Ni compounds such as $[(C_5H_5)_2Mo(\mu\text{-}SBu^t)_2NiC_5H_5]BF_4$ [16] reacts with CuCl and CuI to give light green insoluble substances which do not analyse as $[(C_5H_5)_2Mo(SBu^t)_2CuX]_n$.

A complex of this composition can be obtained, however, if 7 is treated with $[(PMe_3)CuCl]_4$. By following the reaction in $CDCl_3$ in the ^1H NMR, the formation of two products is observed, one of which contains PMe_3 as a ligand. Attempts to separate the two compounds were only partially successful. By using column chromatography, an orange–brown microcrystalline solid **9** was isolated which corresponds to a 1:1 adduct of 7 and CuCl. As molecular weight determinations (in CH_2Cl_2) confirmed that it is a dimer, the structure shown in Scheme 3 can be proposed. It should be mentioned that the dihydride $(C_5H_5)_2MoH_2$ reacts with CuI to give a product of composition $[(C_5H_5)_2MoH_2CuI]_2$ [17] which presumably has a structure similar to **9**.



Scheme 3.

The mechanism proposed for the formation of **9** is shown in Scheme 3. We assume that the reaction of 7 and $[(PMe_3)CuCl]_4$ first leads to **8** which by elimination of PMe_3 gives $[(C_5H_5)_2Mo(\mu\text{-}SBu^t)_2CuCl]$ and finally the isolated dimer. With regard to the relatively low isolated yield of **9**, it seems conceivable that the second product observed in the ^1H NMR spectrum of the reaction mixture is the ionic compound **10** which probably decomposes during chromatography. It can not be decided whether compound **11** (see Scheme 3), isolated in small amounts after chromatography, is formed from **10** or from **8**. **11** has been prepared in much better yield by chloride displacement from $(C_5H_5)_2MoCl_2$ and $NaSBu^t$. The synthesis of an ionic product analogous to **10** has been achieved according to eqn. (4) by using $(C_5H_5)_2Mo(SPh)_2$ as the starting material.

$$(C_5H_5)_2Mo(SPh)_2 + [Cu(CH_3CN)_4]BF_4 + 2PPh_3 \xrightarrow[-2CH_3CN]{} \underset{\textbf{12}}{[(C_5H_5)_2Mo(\mu\text{-}SPh)_2Cu(PPh_3)_2]BF_4} \quad (4)$$

In contrast to the reaction with $[(PMe_3)CuCl]_4$, the bis(thiolato) complex 7 reacts with $CuSBu^t$ to give the dinuclear compound $(C_5H_5)_2Mo(\mu\text{-}SBu^t)_2\text{-}CuSBu^t$ (**13**). In this case, probably for steric reasons, no dimerization occurs. Compound **13** in which the copper is surrounded only by sulfur forms orange crystals which are thermally not very stable and decompose at 47 °C.

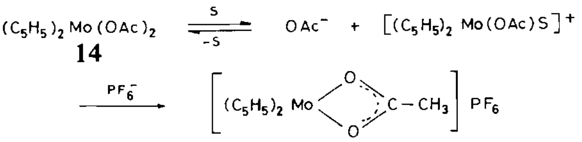
$$7 + CuSBu^t \longrightarrow \underset{\textbf{13}}{(C_5H_5)_2Mo(\mu\text{-}SBu^t)_2CuSBu^t} \quad (5)$$

The goal of preparing new heterometallic Mo–Cu complexes structurally related to **2** in which the two metal atoms are bridged by acetate ligands was attempted by using $(C_5H_5)_2Mo(OAc)_2$ (**14**) as the starting material. The synthesis of the corresponding tungsten compound $(C_5H_5)_2W(OAc)_2$ was recently achieved by Ito and Nakano [18] by treatment of $(C_5H_5)_2WH_2$ with acetic acid in the presence of O_2. On this route, however, only traces of **14** could be obtained [18].

$$(C_5H_5)_2MoCl_2 + 2NaOAc \longrightarrow \underset{\textbf{14}}{(C_5H_5)_2Mo(OAc)_2} + 2NaCl \quad (6)$$

A more rational synthesis of **14** (see eqn. (6)) follows a procedure previously described by Green *et al.* for $(C_5H_5)_2Mo[OC(O)CF_3]_2$ [19]. The bis(acetato) complex is isolated as a blue–grey solid which in acetone forms a deep blue and in methanol a green solution. Although in the mass spectrum the parent molecular ion of **14** has been observed, the conductivity of a nitromethane solution corresponds to that of a 1:1 electrolyte. We therefore assume that in polar solvents S the compound dissociates to form a dicyclopentadienyl monoacetate molybdenum cation and an acetate anion which in the absence of S recombine to give the molecular species.

On addition of NH_4PF_6, the equilibrium shown in eqn. (7) can be completely shifted to the right and an ionic product corresponding to **15** can be isolated in almost quantitative yield. The IR spectrum of the green air-stable compound exhibits two CO stretching frequencies at 1540 and 1450 cm^{-1} which confirm the presence of a chelating acetate unit.



Our attempts to use either **14** or **15** as a building block for the synthesis of heteronuclear complexes such as $(C_5H_5)_2Mo(\mu\text{-}OAc)_2CuX$ (X = Cl, OAc) or

$[(C_5H_5)_2Mo(\mu\text{-}OAc)_2CuL]X$ failed. For example, the reaction of **15** with CuOAc in the presence of triphenylphosphine or 4-methylpyridine only led to the formation of **14** thus indicating that in contrast to $(C_5H_5)_2MoH_2$ [17] and $(C_5H_5)_2Mo(SBu^t)_2$ (see Scheme 3 and eqn. (6)) the corresponding bis(acetato) derivative is not an appropriate chelating ligand for CuX or CuL^+ species.

Experimental

General

All reactions were carried out in dry solvents under nitrogen using Schlenk tube techniques. The starting materials $Na[C_5H_5Mo(CO)_3]$ [20], $[Hg(OAc)(SBu^t)]_n$ [13], $(C_5H_5)_2MoCl_2$ [15], $(C_5H_5)_2Mo(SBu^t)_2$ (7) [16], $(C_5H_5)_2Mo(SPh)_2$ [21], $[(PMe_3)CuCl]_4$ [22], $[Cu(CH_3CN)_4]BF_4$ [23] and $CuSBu^t$* were prepared according to literature methods. Melting points (m.p.) were determined by DTA.

Syntheses

$C_5H_5Mo(CO)_3Hg(\eta^2\text{-}O_2CCH_3)$ (3)

A solution of 837 mg (2.63 mmol) $Hg(OAc)_2$ in 5 ml of benzene was treated with 353 mg (1.31 mmol) $Na[C_5H_5Mo(CO)_3]$ and stirred for 1 h at room temperature. The solution was filtered over Al_2O_3 (activity grade V) and the filtrate was concentrated to *ca.* 1 ml *in vacuo*. Upon addition of pentane, a bright yellow crystalline precipitate was formed which was filtered off, washed with pentane and dried *in vacuo*. Yield: 370 mg (56%); m.p. 73 °C (dec.). *Anal.* Calc. for $C_{10}H_8HgMoO_5$ (505.5): C, 23.96; H, 1.58; Mo, 18.97. Found: C, 24.48; H, 1.72; Mo, 18.26%. ^{1}H NMR (C_6D_6): $\delta(C_5H_5)$ 4.53(s); $\delta(CO_2CH_3)$ 2.25(s, br). IR (KBr): ν(CO) 2005, 1930(sh), 1915, 1580(br), 1420(br) cm^{-1}.

$C_5H_5Mo(CO)_3HgSBu^t$ (6)

A suspension of 303 mg (0.87 mmol) $[Hg(OAc)(SBu^t)]_n$ in 5 ml of benzene was treated with 85 μl (0.88 mmol) 4-methylpyridine and stirred for 30 min at room temperature. The reaction mixture was then treated with 217 mg (0.81 mmol) $Na[C_5H_5Mo(CO)_3]$ and stirred for 1 h. The solution was filtered, concentrated to *ca.* 2 ml *in vacuo* and cooled to 0 °C. Upon addition of pentane, a yellow crystalline precipitate was formed which was filtered off, washed with pentane and dried *in vacuo*. Yield 170 mg (39%); m.p. 105 °C (dec.). *Anal.* Calc. for $C_{12}H_{14}HgMoO_3S$ (535.8): C, 27.13; H, 2.63; Mo, 17.91. Found: C, 27.06; H, 2.40; Mo, 17.87%. ^{1}H NMR (C_6D_6): $\delta(C_5H_5)$ 4.80(s); $\delta(SBu^t)$ 1.65(s, br). IR (KBr): ν(CO) 2002, 1925(sh), 1912 cm^{-1}.

$[(C_5H_5)_2Mo(\mu\text{-}SBu^t)_2CuCl]_2$ (9)

A solution of 227 mg (0.56 mmol) **7** in 20 ml of THF was treated with 98 mg (0.14 mmol) $[(PMe_3)CuCl]_4$. After stirring for 5 min at room temperature a red solution was obtained which was concentrated to *ca.* 10 ml and separated from some insoluble material. The solution was chromatographed on Al_2O_3 (Woelm, neutral, activity grade V) using ethanol as the eluant. First an orange–brown fraction was obtained which upon addition of ether gave an orange–brown microcrystalline precipitate. This was filtered off, repeatedly washed with ether and dried *in vacuo*. Yield 56 mg (20%); m.p. 63 °C (dec.). *Anal.* Calc. for $C_{36}H_{56}Cl_2Cu_2Mo_2S_4$: C, 42.94; H, 5.89; molecular weight 1007.1. Found: C, 42.59; H, 5.89%; M_r 885 (osmometric in CH_2Cl_2). ^{1}H NMR ($CDCl_3$): $\delta(C_5H_5)$ 5.67(s); $\delta(SBu^t)$ 1.34(s, br).

With ethanol/acetone a small amount of a second product was eluted which according to the ^{1}H NMR data proved to be **11** (see below). Yield 15 mg (8%).

$(C_5H_5)_2Mo(SBu^t)Cl$ (11)

A solution of 875 mg (2.95 mmol) **7** in 20 ml THF was treated with 223 mg (2.00 mmol) $NaSBu^t$ and heated for 2 h under reflux. After cooling to room temperature the solvent was removed *in vacuo* and the residue extracted with ether (3 × 5 ml). A green solution was obtained which was brought to dryness *in vacuo* to give a greenish-brown solid. Yield 474 mg (47%); m.p. 78 °C (dec.). *Anal.* Calc. for $C_{14}H_{19}ClMoS$ (341.6): C, 47.92; H, 5.42. Found: C, 47.37; H, 5.66%. ^{1}H NMR ($CDCl_3$): $\delta(C_5H_5)$ 4.92(s); $\delta(SBu^t)$ 1.19(s).

$[(C_5H_5)_2Mo(\mu\text{-}SPh)_2Cu(PPh_3)_2]BF_4$ (12)

A solution of 122 mg (0.39 mmol) $[Cu(CH_3CN)_4]BF_4$ in 5 ml of acetone was treated with 203 mg (0.78 mmol) PPh_3 and stirred for 15 min at room temperature. The solution was then added to a solution of 182 mg (0.39 mmol) $(C_5H_5)_2Mo(SPh)_2$ in 60 ml of acetone. After stirring for 2 h the reaction mixture was filtered and the filtrate was concentrated *in vacuo* to *ca.* 5 ml. Addition of ether led to the formation of a brown oily precipitate which was washed with benzene and ether and recrystallized from CH_2Cl_2/ether to give a brown microcrystalline solid. Yield 393 mg (88%); dec. temp. 121 °C. *Anal.* Calc. for $C_{58}H_{50}BCuF_4MoPS_2$ (1143.4): C, 60.92; H, 4.41; Cu, 5.56; Mo, 8.39. Found: C, 61.39; H, 4.16; Cu, 5.57; Mo, 8.30%. ^{1}H NMR (CD_3NO_2): $\delta(C_5H_5)$ 5.30(s); δ(Ph) 7.14(m).

$(C_5H_5)_2Mo(\mu\text{-}SBu^t)_2CuSBu^t$ (13)

A solution of 154 mg (0.38 mmol) **7** in 15 ml of CH_2Cl_2 was treated with 57 mg (0.37 mmol) $CuSBu^t$

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*$CuSBu^t$ was prepared analogously as described for CuSPh; see ref. 24.

and stirred for 16 h at room temperature. The solution was concentrated *in vacuo* to *ca.* 8 ml and chromatographed on Al_2O_3 (Woelm, neutral, activity grade V). With ethanol an orange fraction was eluted which was concentrated to *ca.* 1 ml *in vacuo*. Upon addition of ether an orange precipitate was obtained which was filtered off and recrystallized from acetone/ether 1/3. Orange moderately air-stable solid; yield 114 mg (56%); m.p. 47 °C. *Anal.* Calc. for $C_{22}H_{37}CuMoS_3$: C, 47.42; H, 6.68; molecular weight 547.1. Found: C, 46.38; H, 6.10; M_r 547 (FD-MS). ^1H NMR ($CDCl_3$): $\delta(C_5H_5)$ 5.67(s); $\delta(CuSBu^t)$ 1.57(br); $\delta(\mu\text{-}SBu^t)$ 1.37(br).

$(C_5H_5)_2Mo(OAc)_2$ *(14)*

A solution of 462 mg (1.14 mmol) $(C_5H_5)_2MoCl_2$ in 20 ml of methanol was treated with 188 mg (2.30 mmol) anhydrous sodium acetate and 50 μl (0.8 mmol) acetic acid. After stirring for 16 h at 40 °C the solvent was removed *in vacuo* and the residue dissolved in 5 ml of acetone. The solution was chromatographed on Al_2O_3 (Woelm, neutral, activity grade V) using acetone as the eluant. A deep blue fraction was collected which was brought to dryness *in vacuo*. The crude product was extracted with ether (3 × 5 ml), the ether solution was filtered and the solvent was removed *in vacuo* to give a blue–grey moderately air-stable solid. Yield 118 mg (30%); m.p. 79 °C (dec.). Molar conductivity: $\Lambda(CH_3NO_2)$ 103.9 $cm^2\ \Omega^{-1}\ mol^{-1}$. The product was characterized by the mass spectrum and IR and ^1H NMR spectroscopic data. MS (70 eV): *m/e* (I_r) 346 (4%; M^+), 303 (8; $M^+ - COCH_3$), 287 (8; $M^+ - CO_2CH_3$), 281 (37; $M^+ - C_5H_5$), 238 (21; $M^+ - C_5H_5 - COCH_3$), 43 (100; CH_3CO^+). IR (KBr): ν(CO) 1595 cm^{-1}. ^1H NMR (CD_3OD): $\delta(C_5H_5)$ 5.78(s), δ(OAc) 2.01(s).

$[(C_5H_5)_2Mo(\eta^2\text{-}O_2CMe)]PF_6$ *(15)*

A solution of 39 mg (0.12 mmol) **14** in 3 ml of methanol was treated with 35 mg (0.21 mmol) NH_4PF_6 and stirred for 30 min at room temperature. A green precipitate was formed which after standing for 1 h was separated from the solution. It was recrystallized from methanol/ether 1/3 to give a green, virtually air-stable solid. Yield 45 mg (88%); dec. temp. 114 °C. *Anal.* Calc. for $C_{12}H_{13}F_6MoO_2P$ (430.2): C, 33.51; H, 3.05. Found: C, 33.22; H, 3.07%. IR (KBr): ν(CO) 1540, 1450 cm^{-1}. ^1H NMR (CD_3OD): $\delta(C_5H_5)$ 5.63(s); δ(OAc) 1.96(s).

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