Inorganica Chimica Acta, 10 (1974) L3–L4

Erratum to Volume 7

Polarized Electronic Spectra of Quadrate Chromium(III) Complexes

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Inorganica Chimica Acta, 7, 685 (1973).

Page 685, line 10 of Introduction, read: $[Cr(en)_2(H_2O)_2]Br_3$

Page 686, line 8 of Results, read: $[Cr(en)_2BrCl]Cl$

Page 690, Acknowledgements, read:

The authors would like to thank Mr. Ed McKnight for building the dewar with some modifications.

Contents of the Letter Section

Cycloheptatriene Dicarbonyltriphenylphosphinemolybdenum(0)

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Received May 9, 1974

Addition of neutral ligands (L) such as amines, phosphines, isocyanides *etc.* to cycloheptatrienemolybdenum tricarbonyl leads to the replacement of the cycloheptatriene ring.[1] This reaction is a convenient route to *fac*-$Mo(CO)_3L_3$ as the only reaction products.[1,2] Only one compound of type $[1,6\text{-}\eta\text{-}C_7H_8M(CO)_2L]$ (M = Mo, Cr; L = 9-phenyl-9-phosphabicylco[4.2.1]nonatriene) has been reported.[3] Substitution of one carbonyl group with L (L = PPh_3, $P(OPh)_3$) has been however achieved in the low temperature photolysis of $[1,6\text{-}\eta\text{-}C_7H_8Cr(CO)_3]$ in the presence of L.[4]

We now report a new route leading to the formation of the molybdenum analog $[1\text{-}6\text{-}\eta\text{-}C_7H_8Mo(CO)_2\text{-}PPh_3]$.

Experimental

Materials

$[1\text{-}6\text{-}\eta\text{-}C_7H_8Mo(CO)_3]$,[5] $[\eta\text{-}C_7H_7Mo(CO)_3]BF_4$,[6] $[\eta\text{-}C_7H_7Mo(CO)_2I]$[7] and $[\eta\text{-}C_7H_7Mo(CO)PPh_3I]$[8] were prepared according to literature methods. All the other products were standard reagent grade and were used without further purification.

Preparation of $[\eta\text{-}C_7H_7Mo(CO)_2PPh_3]BF_4$

PPh_3 (2 mmol) was added slowly to $[\eta\text{-}C_7H_7Mo(CO)_3]BF_4$ (2 mmol) dissolved in 80 ml of a $CHCl_3$/MeOH (1/1 in volume) mixture. The solution was left with stirring for 4 days, then taken to dryness. The crude product was extracted with a THF/CH_2Cl_2 mixture (70/30 in volume) and then precipitated by slow evaporation of CH_2Cl_2 under nitrogen. M.p. 180 - 182 °C dec. Yield $\simeq$ 60%. *Anal.* $C_{27}H_{22}MoPO_2BF_4$ requires C 54.76, H 3.74, P 5.23. Found, C 54.7, H 3.7, P 5.2.

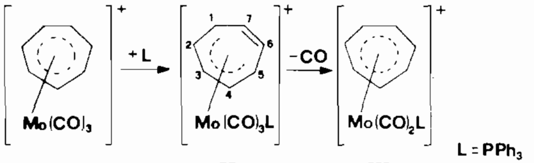
Preparation of [1-6-η-$C_7H_8Mo(CO)_2PPh_3$]

[η-$C_7H_7Mo(CO)_2PPh_3$]BF_4 (2 mmol) suspended in a H_2O/THF system was treated with several small portions of solid $NaBH_4$ until a clear, red THF solution is obtained. The organic layer is then separated, washed with water, dried on Na_2SO_4, and concentrated to a small volume. The product is obtained as red crystals by dilution with ethyl ether. M.p. 145 - 148 °C dec. Yield 95%. *Anal.* $C_{27}H_{23}MoPO_2$ requires C 64.04, H 4.57, P 6.11. Found, C 63.9, H 4.6, P 6.0.

The infrared spectra were recorded with a Perkin–Elmer model 457 spectrophotometer in the region 4000 - 250 cm^{-1} using CsI plates and nujol mulls. The spectra in solution were recorded with KBr cells (1 mm pathlength) with CH_2Cl_2 as solvent. The calibration was performed with a polystyrene film. The accuracy is believed to be within ± 3 cm^{-1}. The N.M.R. spectra were recorded with a Brucker 90 instrument, using TMS as internal standard.

Results and Discussion

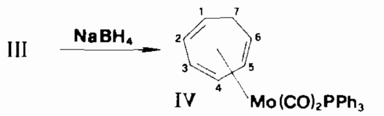
The room temperature reaction of [η-C_7H_7Mo-$(CO)_3$]BF_4 (I) with triphenylphosphine affords good yields of [η-$C_7H_7Mo(CO)_2PPh_3$]BF_4 (III). Identification of III follows from analytical and spectroscopic data. The I.R. spectrum shows two strong ν(CO) absorption at 2023 and 1984 cm^{-1} (in CH_2Cl_2) and characteristic bands of triphenylphosphine and BF_4^- (1058 cm^{-1}) in nujol. The pmr spectrum (in acetone-d_6) shows, in addition to a multiplet for the phenyl protons at $\tau = 2.42$, a doublet ($\tau = 4.0$, J = 2.2 Hz) due to the splitting of the seven equivalent cycloheptatrienyl protons by the phosphorus nucleus. A possible intermediate in this reaction is [1,5-η-$C_7H_7Mo(CO)_3PPh_3$]BF_4 (II) which may lose a CO group to give (III)



I II III

A mechanism involving II (L = MeCN) and [1-3-η-$C_7H_7Mo(CO)_3L_2$]BF_4 as intermediates has been suggested in the kinetic study of the reaction of I with excess of MeCN to give eventually *fac*-[Mo(CO)$_3$-$(MeCN)_3$].[9] *fac*-[Mo$(CO)_3(PPh_3)_3$] is also formed in small amount in our reaction and becomes the only product with excess of triphenylphosphine. III, however, does not react with boiling MeCN, suggesting a stronger bond of the metal with the polyolefin when a carbonyl group is replaced by a phosphine ligand. III can also be obtained from [η-$C_7H_7Mo(CO)_2I$], PPh_3 and $AgBF_4$ although in lower yield (attempts to carry out an analog reaction on [η-$C_7H_7Mo(CO)PPh_3I$] failed). Although [η-$C_7H_7Mo(CO)PPh_3I$] can be easily obtained from [η-$C_7H_7Mo(CO)_2I$] and PPh_3[8] the reaction of III with KI affords only [η-$C_7H_7Mo(CO)_2I$]

[η-$C_7H_7Mo(CO)_2PPh_3$]BF_4 (III) can be easily converted into [1-6η-$C_7H_8Mo(CO)_2PPh_3$] (IV) by reduction with $NaBH_4$:



The I.R. spectrum of IV shows two equally intense ν(CO) absorptions at 1908 and 1824 cm^{-1} (in CH_2Cl_2). The pmr spectrum in $CDCl_3$ has multiplets at $\tau = 2.74$ (PPh_3), 4.42 (H_3, H_4), 5.40 (H_2, H_5), 7.04 (H_1, H_6) and 7.74 - 8.31 (H_7, $H_{7'}$, overlapping). These signals are shifted upfield in comparison with those of [1-6-η-$C_7H_8Mo(CO)_3$]. The same trend occurs in the corresponding chromium complexes[4] and reflects an increased electron density on the polyolefin upon substitution of a CO group with the phosphine. Substitution of the cycloheptatriene ring by nitriles cannot be achieved in the substituted phosphine complexes, thereby supporting the view that a stronger back-bonding from the metal to the polyolefin is responsible for the upfield shift in the pmr spectrum of IV.

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