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Preliminary communication

π-HETEROCYCLE METAL COMPLEX CHEMISTRY: SYNTHESIS OF η^6-(2,6-DIMETHYLPYRIDINE) (TRIPHENYLPHOSPHINE) DICARBONYLCHROMIUM AND RELATED COMPLEXES

HENRY W. CHOI* and MARK S. SOLLBERGER
Occidental Research Corporation, 2100 S.E. Main Street, Irvine, CA 92714 (U.S.A.)

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Summary

π-(2,6-Dimethylpyridine)(triphenylphosphine)dicarbonylchromium was prepared by the photochemical reaction of π-(2,6-dimethylpyridine)tricarbonylchromium with triphenylphosphine. Analogously, π-(2,4,6-trimethylpyridine)-(triphenylphosphine)dicarbonylchromium, π-(2,6-dimethylpyridine)(trimethyl phosphite)dicarbonylchromium, and π-(2,6-dimethylpyridine)bis(trimethyl phosphite)carbonylchromium were prepared. The phosphorus ligand substituted complexes were thermally more robust than their tricarbonyl analogs and showed a drastic inhibition toward arene exchange reactions.

Aromatic nitrogen heterocycles have received renewed interest from energy intensive research efforts due to their preponderance in alternative energy sources such as shale oil [1—3]. Interactions of pyridine-type compounds with metals may be important, if not critical, in hydrodenitrogenation processes used for upgrading fuels. Although the σ-interaction of pyridines with transition metals has been well established, to date only six π-pyridine-type metal complexes have been reported [4]. Our modifications to the preparation of organometallic π-heterocycle arene complexes have enabled the isolation in large quantities of 2,6-dimethyl- and 2,4,6-trimethylpyridine(tricarbonylchromium) with which several derivative complexes were prepared and their chemistry explored.

η^6-($Me_2C_5H_3N$)Cr(CO)$_3$ (1) was prepared by the reaction of (CH_3CN)$_3$Cr(CO)$_3$ with 2,6-dimethylpyridine in dioxane solution for 14 h at 60°C (ca. 60% yield based on Cr) [5]. The liberated CH_3CN was removed periodically by evacuation since the desired product is stoichiometrically decomposed by it. We found 1 to be reactive toward most donor solvents, including pyridine and THF, and NMR spectroscopy revealed that uncoordinated 2,6-dimethylpyridine was generated

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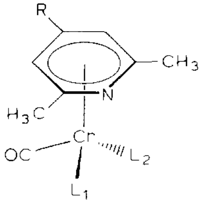

(1, R = H ; L_1 = L_2 = CO ;
2, R = H ; L_1 = CO , L_2 = PPh_3 ;
3, R = CH_3 ; L_1 = CO , L_2 = PPh_3 ;
4, R = H ; L_1 = L_2 = $P(OMe)_3$;
5, R = H ; L_1 = CO , L_2 = $P(OMe)_3$)

in these decompositon reactions. Benzene solutions of **1** when heated to 80° C generated η^6-(benzene)tricarbonylchromium and 2,6-dimethylpyridine. Facile arene exchange seems to be a general property of η^6-(heterocycle)tricarbonylchromium complexes. Dimethylpyridine solutions of η^6-(2,4,6-trimethylpyridine)tricarbonylchromium, which was prepared in an analogous procedure to **1**, upon warming generated **1** and free trimethylpyridine.

Although the heterocyclic arene ligand was invariably lost in thermally activated reactions (a reactivity pattern consistent with carbocyclic arenes), the photochemical activation of η^6-(heterocycle)tricarbonylchromium led to the selective labilization of the carbon monoxide. At 0° C, yellow methylcyclohexane solution of **1** when irradiated in the presence of PPh_3 with a quartz filtered mercury lamp (450 W) for 1 h was transformed to red. When triphenylphosphine was added slowly during photolysis, the product mixture contained the mono-substituted phosphine complex, η^6-$(Me_2C_5H_3N)Cr(CO)_2PPh_3$ (**2**) [6], which was isolated after silica gel column chromatography as orange-red crystals in ca. 40% yield (based on **1**). The 200 MHz ^1H NMR spectrum showed the characteristic upfield shifting of the ring protons. The $^{31}P\{^1H\}$NMR (C_6D_6, 81 MHz) spectrum consisted of a singlet resonance at δ 86.6 ppm. This large downfield shifting of the triphenylphosphine resonance upon coordination is not unusual and is comparable to η^6-$(C_6H_6)Cr(CO)_2PPh_3$ ^{31}P chemical shift observed at δ 91.1 ppm in carbon disulfide [8].

The air stable orange-red crystals of **2** were thermally more robust than **1** decomposing at 180° C (as compared to 137° C). The increase in stability of the arene complex upon phosphorus substitution was also evident in the drastic retardation of the arene exchange process, where benzene solutions of **2** showed no arene exchange when heated to 140° C for several hours. This tendency was also observed for phosphorus ligand substituted carbocyclic arene complexes [9].

The photolysis procedure for the preparation of triphenylphosphine derivatives was shown to be effective for other η^6-heterocycle complexes by the synthesis of η^6-(2,4,6-trimethylpyridine)(triphenylphosphine)dicarbonylchromium (**3**) [10] from η^6-$(Me_3C_5H_2N)Cr(CO)_3$ and PPh_3. In these photochemical reactions with triphenylphosphine, addition of excess ligand to the reaction mixture did not result in the formation of a bis-phosphine substituted arene complex but did result in the increased formation of a side-product,

$Cr(CO)_4(PPh_3)_2$. Reactions of the smaller trimethyl phosphite ligand with 1 generated as the major product the di-substituted η^6-($Me_2C_5H_3N$)-Cr(CO)-$[P(OMe)_3]_2$ (4) and a lesser amount of the mono-substituted η^6-($Me_2C_5H_3N$) $Cr(CO)_2[P(OMe)_3]$ (5), which were characterized by mass spectroscopy, and by ^{1}H and $^{31}P\{^1H\}$NMR spectroscopy [11]. Attempted isolation of these phosphite complexes rendered red oils which were mixtures of the two.

We anticipate that the chemistry of phosphorus ligand stabilized π-(heterocycle)chromium complexes should be extensive, especially in protonation reactions. Synthesis strategies for π-heterocycle complexes of other metals are being examined.

References and notes

1 S.F. Culberson, and P.D. Rolniak, Oil & Gas J., (1981) 43.

2 D. Hardy, R.N. Hazelett and J. Solash, Prepr. Div. Fuel Chem., 27 (1982) 201.

3 J.F. Cocchetto and C.N. Satterfield, Ind. Eng. Chem. Process Des. Dev. 15 (1976) 272.

4 All are complexes of chromium: $(C_5H_5N)Cr(PF_3)_3$ was briefly mentioned by P.L. Timms, Angew. Chem., Int. Ed. Engl., 14 (1975) 273. Four are $Cr(CO)_3$ derivatives of dimethyl-, trimethyl-, tetramethyl-, and pentamethyl-pyridine: H.G. Biedermann, K. Öfele, and J. Tajtelbaum, Z. Naturforsch. B, 31 (1976) 321; H.G. Biedermann, K. Öfele, N. Schuhbauer and J. Tajtelbaum, Angew. Chem., Int. Ed. Engl., 14 (1975) 639; $(Me_2C_5H_3N)_2Cr$ was reported by L.H. Simons, P.E. Riley, R.E. Davis, and J.J. Lagowski, J. Am. Chem. Soc., 98 (1976) 1044, P.E. Riley and E. Davis, Inorg. Chem. 15 (1976) 2735.

5 The main problem we encountered in following the reported procedure [4] was in the sublimation of $Cr(CO)_6$ away from the reaction mixture which resulted in low yields (based on Cr initially present).

6 2: Mass Spectrum (EI): 477 *m/e* for ^{52}Cr isotope. Anal. Calcd.: C, 67.9; H, 5.1; N, 2.9; P, 6.5 $C_{27}H_{24}$-$CrNO_2P$. Found: C, 67.3; H, 5.1; N, 2.8; P, 6.3%. ^{1}H NMR (C_6D_6, 200 MHz): δ 7.7 and 7.1 ppm (m, 15H, PPh_3), 4.9 ppm (t, 1 *para*-H, *J*(HH) 6.2 Hz, *J*(HP) not observed [7]), 4.1 ppm (d, 2 *meta*-H, *J*(HH) 6.1 Hz), 1.9 ppm (s, 6 methyl-H).

7 When observable, *J*(HP) is usually small: 3.5 Hz for $(C_6H_6)Cr(CO)_2PPh_3$, and 1.7 Hz for (1,3,5-$Me_3C_6H_3$)$Cr(CO)_2PPh_3$, D.N. Kursanov, V.N. Setkina, P.V, Petrovskii, V.I. Zdanovich, N.K. Baranetskaya and I.D. Rubin, J. Organometal. Chem., 37 (1972) 339.

8 L.A. Fedorov, P.V. Petrovskii, E.I. Fedin, N.K. Baranetskaya, V.I. Zdanovich, V.N. Setkina and D.N. Kursanov, J. Organometal. Chem., 99 (1975) 297.

9 M.F. Semmelhack, W. Seufert and L. Keller, J. Organometal. Chem., 226 (1982) 183.

10 3: m.p. 190°C (dec.). Mass spectrum (EI): 491 *m/e* for ^{52}Cr isotope. ^{1}H NMR (C_6D_6, 200 MHz): δ 7.7 and 7.1 ppm (m, 15H, PPh_3), 4.0 ppm (s, 2 *meta*-H), 2.0 ppm (s, 3 *para*-CH_3), 1.9 ppm (s, 6 *ortho*-CH_3). $^{31}P\{^1H\}$NMR (C_6D_6, 81 MHz): δ 86.7 ppm (s).

11 4: Mass spectrum (EI): 435 *m/e* for ^{52}Cr isotope. ^{1}H NMR (C_6D_6, 200 MHz): δ 4.9 ppm (approximate triplet of triplets, 1 *para*-H, J_{HH} = 5.9 Hz, J_{HP} = 4.4 Hz), 4.3 ppm (doublet of triplets, 2 *meta*-H, *J*(HH) 6.0 Hz, *J*(HP) 2.2 Hz), 3.4 ppm (filled-in doublet, 18H, $P(OMe)_3$, *J*(HP) 10.9 Hz), 2.3 ppm (s, 6 methyl-H). $^{31}P\{^1H\}$NMR (C_6D_6, 81 MHz): δ 216.4 ppm (s).
5: Mass spectrum (EI): 339 *m/e* for ^{52}Cr isotope. ^{1}H NMR (C_6D_6, 200 MHz): δ 4.9 ppm (*para*-H, partially obscured by 4), 4.4 ppm (dd, *meta*-H, *J*(HH) 6.4 Hz, *J*(HP) 2.0 Hz), 3.5 ppm (d, $P(OMe)_3$, *J*(HP) 9.9 Hz), 2.4 ppm (s, methyl-H). $^{31}P\{^1H\}$NMR (C_6D_6, 81 MHz): δ 213.7 ppm (s).