

Preliminary communication

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

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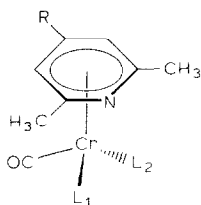
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Summary

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 -(Me₂C₅H₃N)Cr(CO)₃ (1) was prepared by the reaction of (CH₃CN)₃Cr(CO)₃ with 2,6-dimethylpyridine in dioxane solution for 14 h at 60°C (ca. 60% yield based on Cr) [5]. The liberated CH₃CN 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



- (1, R = H ; L₁ = L₂ = CO ;
 2, R = H ; L₁ = CO , L₂ = PPh₃ ;
 3, R = CH₃ ; L₁ = CO , L₂ = PPh₃ ;
 4, R = H ; L₁ = L₂ = P(OMe)₃ ;
 5, R = H ; L₁ = CO , L₂ = P(OMe)₃)

in these decomposition 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 PPh₃ 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 -(Me₂C₅H₃N)Cr(CO)₂PPh₃ (**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 ³¹P{¹H}NMR (C₆D₆, 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 -(C₆H₆)Cr(CO)₂PPh₃ ³¹P 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 -(Me₃C₅H₂N)Cr(CO)₃ and PPh₃. 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,

$\text{Cr}(\text{CO})_4(\text{PPh}_3)_2$. Reactions of the smaller trimethyl phosphite ligand with 1 generated as the major product the di-substituted $\eta^6\text{-(Me}_2\text{C}_5\text{H}_3\text{N)-Cr}(\text{CO})\text{-[P(OMe)}_3\text{]}_2$ (4) and a lesser amount of the mono-substituted $\eta^6\text{-(Me}_2\text{C}_5\text{H}_3\text{N)Cr}(\text{CO})_2\text{[P(OMe)}_3\text{]}$ (5), which were characterized by mass spectroscopy, and by ^1H and $^{31}\text{P}\{^1\text{H}\}$ 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

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- 3 J.F. Cocchetto and C.N. Satterfield, *Ind. Eng. Chem. Process Des. Dev.* 15 (1976) 272.
- 4 All are complexes of chromium: $(\text{C}_5\text{H}_5\text{N})\text{Cr}(\text{PF}_3)_3$ was briefly mentioned by P.L. Timms, *Angew. Chem., Int. Ed. Engl.*, 14 (1975) 273. Four are $\text{Cr}(\text{CO})_3$ 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; $(\text{Me}_2\text{C}_5\text{H}_3\text{N})_2\text{Cr}$ 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 $\text{Cr}(\text{CO})_6$ 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 $\text{C}_{27}\text{H}_{24}\text{CrNO}_2$. Found: C, 67.3; H, 5.1; N, 2.8; P, 6.3%. ^1H NMR (C_6D_6 , 200 MHz): δ 7.7 and 7.1 ppm (m, 15H, PPh_3), 4.9 ppm (t, 1 *para*-H, $J(\text{HH})$ 6.2 Hz, $J(\text{HP})$ not observed [7]), 4.1 ppm (d, 2 *meta*-H, $J(\text{HH})$ 6.1 Hz), 1.9 ppm (s, 6 methyl-H).
- 7 When observable, $J(\text{HP})$ is usually small: 3.5 Hz for $(\text{C}_6\text{H}_5)_2\text{Cr}(\text{CO})_2\text{PPh}_3$, and 1.7 Hz for $(1,3,5\text{-Me}_3\text{C}_6\text{H}_3)_2\text{Cr}(\text{CO})_2\text{PPh}_3$, 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.
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- 10 3: m.p. 190°C (dec.). Mass spectrum (EI): 491 m/e for ^{52}Cr isotope. ^1H 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). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 81 MHz): δ 86.7 ppm (s).
- 11 4: Mass spectrum (EI): 435 m/e for ^{52}Cr isotope. ^1H NMR (C_6D_6 , 200 MHz): δ 4.9 ppm (approximate triplet of triplets, 1 *para*-H, $J_{\text{HH}} = 5.9$ Hz, $J_{\text{HP}} = 4.4$ Hz), 4.3 ppm (doublet of triplets, 2 *meta*-H, $J(\text{HH})$ 6.0 Hz, $J(\text{HP})$ 2.2 Hz), 3.4 ppm (filled-in doublet, 18H, P(OMe)_3 , $J(\text{HP})$ 10.9 Hz), 2.3 ppm (s, 6 methyl-H). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 81 MHz): δ 216.4 ppm (s).
5: Mass spectrum (EI): 339 m/e for ^{52}Cr isotope. ^1H NMR (C_6D_6 , 200 MHz): δ 4.9 ppm (*para*-H, partially obscured by 4), 4.4 ppm (dd, *meta*-H, $J(\text{HH})$ 6.4 Hz, $J(\text{HP})$ 2.0 Hz), 3.5 ppm (d, P(OMe)_3 , $J(\text{HP})$ 9.9 Hz), 2.4 ppm (s, methyl-H). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 81 MHz): δ 213.7 ppm (s).