Journal of Organometallic Chemistry, 217 (1981) 179—182
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

A NEW HETEROCYCLIC LIGAND FOR TRANSITION METALS: 1,4,5,8,9,12-HEXAAZATRIPHENYLENE AND ITS CHROMIUM CARBONYL COMPLEXES

R. NASIELSKI-HINKENS *, M. BENEDEK-VAMOS *, D. MAETENS and J. NASIELSKI

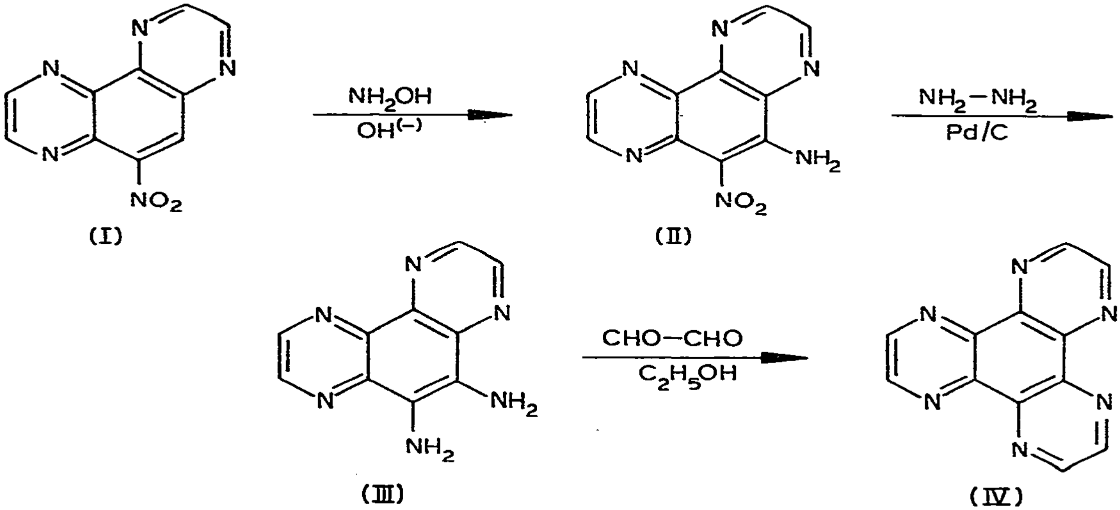
Université Libre de Bruxelles, Service de Chimie Organique, Faculté des Sciences, C.P. 160, Av. F.D. Roosevelt, 50 1050 Bruxelles (Belgium)

(Received February 9th, 1981)

Summary

The synthesis of 1,4,5,8,9,12-hexaazatriphenylene (HAT), a new ligand for low-valent transition metals, is described; it gives mono-, bis- and tris-chromium tetracarbonyl complexes. The CO stretching frequencies in (HAT)Cr(CO)$_4$ show that HAT is a stronger electron acceptor than 1,10-phenanthroline.

Continuing our investigations on complexing properties [1] of 1,4,5,8-tetraazaphenanthrene (TAP) and substituted derivatives, we undertook the synthesis of a new heterocyclic system, viz. dipyrazino[2,3-*f*][2′,3′-*h*]quinoxaline or 1,4,5,8,9,12-hexaazatriphenylene (IV) (hereafter abbreviated as HAT). This was synthesized in three steps from 9-nitro-TAP (I) [2].



---

* Deceased on 21 April 1980.

II was prepared from I by a classical amination [3]. After reduction and further condensation of III with aqueous glyoxal, HAT (IV) was obtained with an overall yield of 34% based on 9-nitro-TAP (I). IV was suspended in benzene and irradiated in the presence of three equivalents of chromium hexacarbonyl [1]. After 20 hours irradiation, the mixture contains three different blue complexes easily separable by column chromatography.

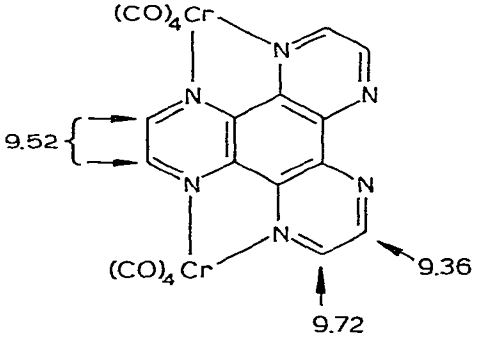
$$\mathrm{HAT} \xrightarrow[C_6H_6/h\nu]{CrCO_6} Cr_3(CO)_{12}(HAT) + Cr_2(CO)_8(HAT) + Cr(CO)_4(HAT)$$

Elution gave 30% of $Cr_3(CO)_{12}(HAT)$, 20% of $Cr_2(CO)_8(HAT)$, 5% of $Cr(CO)_4$-(HAT) and 38% of unchanged HAT.

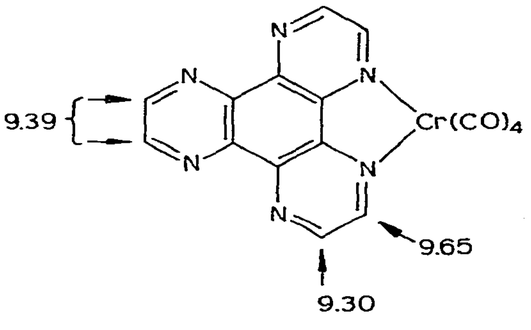
It is noteworthy that the di- and trimetallic complexes are formed in the highest yields; this is due to the fact that the mono- and dimetallic complexes are much more soluble than the free ligand, and are thus available for trapping the photogenerated $Cr(CO)_5$. This was demonstrated as follows. $Cr(CO)_6$ in degassed THF was photolysed, and the resulting yellow solution of $Cr(CO)_5$-(THF) was added to a chloroform solution of one equivalent of HAT. After 12 hours at room temperature, work-up gave, in addition to 50% of recovered ligand, 40% of $Cr(CO)_4(HAT)$, 5% of $Cr_2(CO)_8(HAT)$ and only traces of the trimetallic complex. The structure of these new chelates was established from IR and ^{1}H NMR data.

The trimetallic complex $Cr_3(CO)_{12}(HAT)$ is pale blue-green, whereas the other two are deep blue. It is also eluted first from silica gel by ethyl acetate/hexane (30/70). These qualitative properties point to a highly symmetrical and non-polar system. The ^{1}H NMR spectrum shows only a sharp singlet at 9.56 ppm (TMS; DMSO-d_6); all protons are thus equivalent. Four carbonyl IR bands are found at 1995, 1935, 1915 and 1865 cm^{-1} ($CHCl_3$) as expected for local C_{2v} symmetry.

The dimetallic complex $Cr_2(CO)_8(HAT)$ is dark blue. The ^{1}H NMR spectrum shows a singlet at 9.52 ppm (2 H), and two doublets at 9.36 and 9.72 ppm, each integrating for 2 H and with a coupling of 3.0 Hz. This spectrum is in agreement with structure V.



(V)



(VI)

Despite several purifications, this compound showed five IR bands at 2010, 1995, 1935, 1915 and 1865 cm^{-1} ($CHCl_3$). Some coupling between the $Cr(CO)_4$ moieties must thus be assumed; further analysis has not been attempted.

TABLE 1

CARBONYL STRETCHING FREQUENCIES (in $CHCl_3$) AND CALCULATED FORCE CONSTANTS FOR $Cr(CO)_4L$

L	ν(CO) (cm^{-1})				$k_{ax.}$(CO) (Nm^{-1}) [b]	$k_{eq.}$(CO) (Nm^{-1}) [c]
	axial	equatorial				
phen	2008	1907	1883	1831	1539	1409
TAP [a]	2013	1926	1910	1857	1558	1447
HAT	2010	1930	1915	1860	1559	1452

[a] The values for $Cr(CO)_4TAP$ have been remeasured with a higher accuracy; they differ slightly from those given in ref. 1. [b] ±1 Nm^{-1}. [c] ±4 Nm^{-1}.

The blue-violet monometallic complex is eluted last. The ^{1}H NMR spectrum shows one singlet at 9.39 ppm (2 H), and two doublets (J = 3.0 Hz) at 9.30 and 9.65 ppm, each integrating for 2 H. This spectrum is in agreement with structure VI. There are four carbonyl stretchings found at 2010, 1930, 1915 and 1860 cm^{-1} ($CHCl_3$), as expected for local C_{2v} symmetry.

A comparison of the electronic properties of three chelating ligands, 1,10-phenanthroline, tetraazaphenanthrene and hexaazatriphenylene is possible on the basis of their carbonyl stretching frequencies. Table 1 lists the relevant frequencies and the corresponding force constants found by the Cotton-Kraihanzel force field. The values show that HAT is a slightly better electron acceptor than TAP, both being stronger acceptors than phenanthroline.

Experimental

The IR spectra in the CO stretching region were recorded on a Perkin-Elmer 357 spectrometer. Proton magnetic resonance spectra were determined on a Jeol 100 spectrometer. Chemical shifts are reported as δ units in ppm with tetramethylsilane as internal standard.

9-Amino-10-nitro-TAP (II)

9-Nitro-TAP (4.04 g; 17 mmol) was dissolved in the minimal amount of hot ethanol/dioxane (60/40 v/v). The solution was cooled rapidly with stirring, to give a fine suspension. Powdered hydroxylamine hydrochloride (7.5 g; 108 mmol) was introduced and potassium hydroxide (8.0 g; 142 mmol in 90 ml of methanol) was then added to the cooled mixture. Stirring was maintained for 0.5 h at 0°C and 1 h at room temperature. The resulting brown suspension was poured into ice-water. After one night, the yellow precipitate (2.8 g) was removed, rinsed with water then methanol, and dried; 9-amino-10-nitro-1,4,5,8-tetraazaphenanthrene (II) obtained in 65% yield was used without further purification.

9,10-Diamino-TAP (III)

A solution of hydrazine hydrate 98% (5 ml) in 20 ml ethanol/dioxane (1/1) was added dropwise during 1.5 h to a hot suspension of powdered compound II (2.0 g; 8 mmol) in 300 ml ethanol/dioxane containing 1.5 g of Pd/C (10%).

The mixture was then refluxed until the starting material has disappeared (TLC), and was then filtered hot, to give red needles on cooling. The filtrate was evaporated to dryness and the residue triturated with water. The total yield of 9,10-diamino-TAP (1.4 g) was 80%. An analytical sample was recrystallized from ethanol, m.p. 270—310°C (dec). Found: C, 56.7; H, 3.9; N, 39.6 (mol.wt. 212.2). $C_{10}H_8N_6$ calcd.: C, 56.6; H, 3.8; N, 39.6%. ^1H NMR (DMSO-d_6): H(2), H(7): 8.88 ppm (d); H(3), H(6): 8.97 ppm (d); J(H,H) = 2.0 Hz.

1,4,5,8,9,12-Hexaazatriphenylene (IV)

Diamine III (1.4 g; 6 mmol) was added to a boiling mixture of 150 ml of ethanol with 20 ml of acetic acid. Glyoxal (2 ml of a 30% aqueous solution) was added dropwise and the suspension slowly disappeared. After a few minutes a brown solid suddenly separated, and this was removed after cooling. It was continuously extracted for 24 h with 500 ml of boiling chloroform, and the chloroform solution was treated with charcoal and filtered through a thin layer of silica gel. Evaporation of the solvent gave the HAT (1.04 g; 65%) as a powder. M.p. >350°C. An analytical sample recrystallized from water/acetic acid (7/3) gave white needles. Found: C, 61.4; H, 2.6; N, 35.8 (mol.wt. 234.2). $C_{12}H_6N_6$ calcd.: C, 61.5; H, 2.6; N, 35.9%. ^1H NMR ($CDCl_3$): 9.30 ppm (s). Mass spectrum: $m/z = 234$.

The metallic complexes of HAT were prepared using the experimental conditions described previously [1]. The separation was performed on silica gel (0.063—0.02 mm) with a mixture of ethylacetate/n-hexane (30/70). Unchanged ligand was eluted with boiling chloroform.

Acknowledgement

We are grateful to the Institut pour l'Encouragement de la Recherche Scientifique dans l'Industrie et l'Agriculture (IRSIA) for award of a fellowship to one of us (D.M.).

References

1 D. Maetens, J. Nasielski and R. Nasielski-Hinkens, J. Organometal. Chem., 168 (1979) 177.
2 R. Nasielski-Hinkens, M. Benedek-Vamos and D. Maetens, J. Heterocyclic Chem., 17 (1980) 873.
3 R. Nasielski-Hinkens, M. Benedek-Vamos, J. Chem. Soc. Perkin I. (1975) 1229.