Journal of Organometallic Chemistry, 107 (1976) C27—C30

Preliminary communication

RHODIUM(I) AND IRIDIUM(I) CARBONYL COMPLEXES WITH 1,3-BIS(ARYLIMINO)ISOINDOLINES

WALTER O. SIEGL

Research Staff, Ford Motor Company, Dearborn, Michigan 48121 (U.S.A.)

(Received October 31st, 1975)

Summary

The first metal carbonyl complexes with the uninegative tridentate 1,3-bis(arylimino)isoindoline (BAII) ligand have been prepared. Rhodium(I) forms a 4-coordinate complex of the type RhL(CO) and iridium(I) a 5-coordinate $IrL(CO)_2$ complex. Changes in remote substituents on the BAII ligand are reflected in changes in the metal carbonyl stretching frequencies demonstrating the ability to selectively modify the electron density at the metal center. The coordinatively unsaturated RhL(CO) is quite reactive toward oxidative addition; stable alkyl- and acyl-rhodium(III) complexes have been prepared and isolated.

Reported herein are the first d^8 and d^6 transition metal carbonyl complexes with the unique 1,3-bis(arylimino)isoindoline (BAII) ligand system [1-3]. The chemistry of low valent rhodium and iridium complexes with new ligand systems continues to be of interest because of the well recognized catalytic properties of these metal ions and the recently uncovered biological activity of rhodium with certain nitrogen-donor ligands [4]. The potential to modify their donor properties without introducing significant changes in coordination geometry stimulated our interest in the BAII ligands. We found that a number of BAII ligands form stable carbonyl complexes with rhodium(I) and iridium(I); their preparation, characterization, and some preliminary reactivity studies are presented below.

The BAII ligand system is a uninegative, or less frequently a neutral, tridentate ligand with three N-donor sites. Unlike the polypyrazolylborates, the only extensively studied mononegative tridentate N-donor ligands [5], the BAII's are expected to prefer a planar configuration with the three conjugated donor nitrogen atoms coplanar with the metal center. Prepared from phthalonitrile and a primary aromatic amine [1,6], the BAII may be conveniently modified by varying the amine; differences in donor, steric, and physical (e.g., solubility) properties resulting from such modifications have been observed for both ligand and metal complex [7].

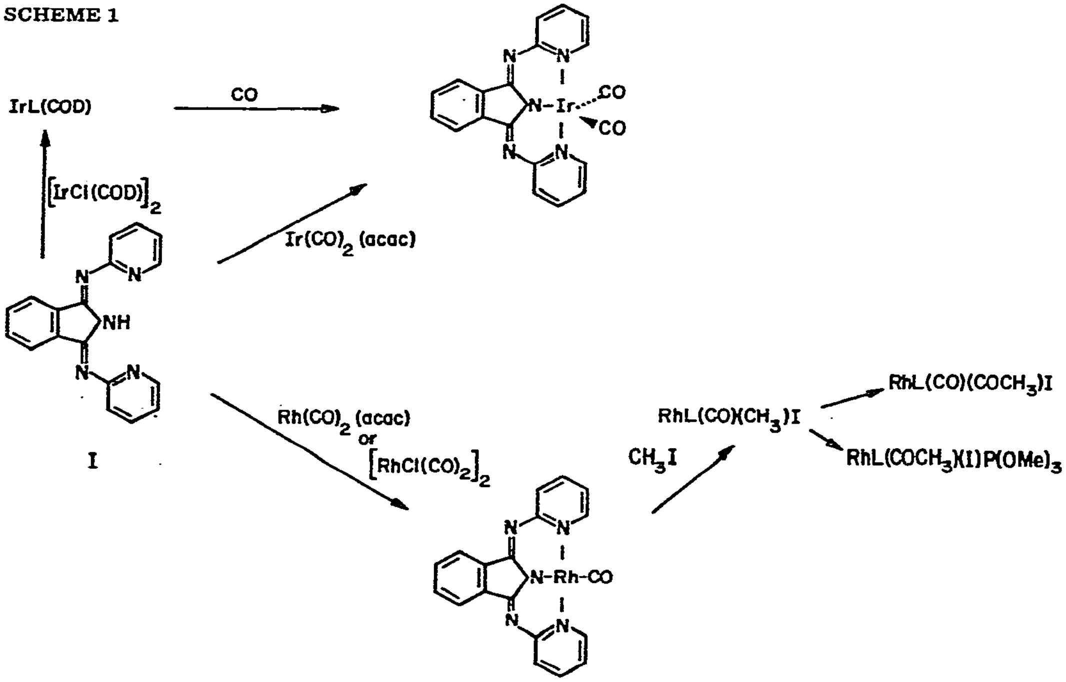
Preparation and stability

The BAII ligand, 1,3-bis(2-pyridylimino)isoindoline, (I) reacts readily with $Ir(CO)_2(acac)$* in the presence of a catalytic amount of DABCO (1,4-diazabicyclo[2.2.2]octane) to afford in good yield a stable dicarbonyl in which the σ-donor acetylacetonate anion has been replaced by the σ-donor BAII anion as shown in Scheme 1. Although moderately air-sensitive in solution the coordinatively saturated dicarbonyl complex is air-stable in the solid state. The reaction with $Ir(CO)_2(acac)$ is general for a variety of substituted BAII where the pyridine rings bears substituents or has been replaced by another aromatic heterocyclic as shown in Table 1. The preparation of a 5-coordinate $IrL'(CO)_2$ complex failed only when methyl substituents were present α to the pyridyl nitrogens (e.g., 6-position on the pyridine ring of I) thus hindering the approach of the metal ion to the coordination sites.

The BAII ligands did not react with $IrCl(CO)(PPh_3)_2$ under mild conditions but did react with $[IrCl(COD)]_2$ to form the BAII-COD complex IrL(COD). This presumably 5-coordinate COD complex reacted rapidly with CO to afford the dicarbonyl complex as described in Scheme 1.

Treatment of the BAII ligand I with either $Rh(CO)_2(acac)$ and a catalytic amount of DABCO or $[RhCl(CO)_2]_2$ and one equivalent of DABCO led to formation of the apparently square planar rhodium(I) mono-carbonyl complex RhL(CO)*. The preference of rhodium(I) for 4-coordination versus that of iridium(I) for 5-coordination has been observed with certain other multidentate ligand systems [8]. The preparation of RhL(CO) appears to be general

SCHEME 1



---

* At room temperature in CH_2Cl_2 or $CHCl_3$ the reaction time is 24 hours or less.

TABLE 1

NEW RHODIUM AND IRIDIUM COMPLEXES WITH BAII LIGANDS

Complex	Ligand derived from [a]	Color	ν(CO) [b]	Yield (%)
RhL(CO)	2-Aminopyridine	Rust	1951	72
RhL′(CO)	2-Amino-4-methylpyridine	Red-Brown	1936	72
RhL′(CO)	2-Aminopyrazine	Brown	1958	77
RhL′(CO)	2-Amino-5-nitropyridine	Brown	1972	Low [c]
RhL′(CO)(CH_3)I	2-Amino-4-methylpyridine	Orange-Red	2056	93
RhL′(CO)($COCH_3$)I	2-Amino-4-methylpyridine	Rust	2088 [d]	74
RhL′($COCH_3$)(I)P($OMe)_3$	2-Amino-4-methylpyridine	Orange	— [e]	21
IrL($CO)_2$	2-Aminopyridine	Yellow-Orange	2047, 1968	50
IrL′($CO)_2$	2-Amino-4-propylpyridine	Brown	2052, 1984	84
IrL′($CO)_2$	2-Aminothiazole	Red-Brown	2052, 1974	79
IrL′($CO)_2$	2-Amino-5-chloropyridine	Red-Brown	2060, 1974	60
IrL′($CO)_2$	2-Amino-5-nitropyridine	Dark-Brown	2078, 2003	97
IrL(COD)	2-Aminopyridine	Brown	—	78

[a] Ligand derived from this amine and phthalonitrile. [b] KBr pellets. [c] Was not separated from unreacted ligand due to low solubility. [d] Acyl: 1586 and 1578. [e] Acyl: 1576.

for a number of BAII ligands although as in the iridium(I) case the preparation fails with methyl substituents in the 6-pyridyl positions of I.

The rhodium(I) mono-carbonyl complex is unreactive toward excess CO but is reactive toward O_2 even in the solid state. In solution, treatment with O_2 led to rapid formation of an as yet uncharacterized material which exhibits no carbonyl bands.

Spectra and physical properties

The ability to influence the donor properties of L by making substituent changes on the aryl groups of the BAII ligand is shown in Table 1. Electron-withdrawing substituents at remote sites on the ligand shift the metal carbonyl stretching frequencies to higher wave numbers, an observation consistent with reduced electron density at the metal center.

A major reason for the lack of attention afforded BAII type ligands in the past may lie with the relatively low solubilities associated with metal complexes of the simple BAII ligands such as I. We observed that the introduction of alkyl substituents (methyl, ethyl, n-propyl, etc.) in the 4-position of the pyridyl ring of I significantly increases the solubility of the corresponding metal complexes in organic solvents. The iridium dicarbonyl complex with electron-withdrawing substituents (Cl or NO_2) on the pyridyl ring is only very sparingly soluble in CH_2Cl_2, whereas the unsubstituted complex is modestly soluble and the 4-n-propyl derivative is highly soluble even in a non-polar solvent such as benzene.

Reactivity toward alkyl and acyl halides

As might be expected the coordinatively saturated 5-coordinate IrL($CO)_2$ was considerably less reactive toward oxidative addition than was the coordinatively unsaturated RhL(CO). Unreactive toward methyl iodide at room temperature, the iridium dicarbonyl complex reacted with acetyl chloride, not to give a simple oxidative addition adduct but to undergo decomposition to a product containing no terminal CO groups.

The square planar RhL(CO) exhibits a chemical reactivity similar to that of some of the phosphine carbonyl complexes of rhodium(I). For example, RhL(CO) reacts rapidly with methyl iodide (CH_2Cl_2, 25°C) to yield the corresponding rhodium(III) oxidative addition adduct (ν(CO) 2056 cm^{-1}). Migratory insertion of CO in the methyl—rhodium bond occurs upon treatment with CO to afford the corresponding acyl complex (ν(CO) 2088 cm^{-1}). Upon treatment with trimethylphosphite the corresponding trimethylphosphite substituted acyl complex is obtained as shown in Scheme 1.

Spectral data and elemental analyses obtained for the new ligands and metal complexes supported the structures assigned in Table 1.

The preparation and isolation of RhL(CO) and $IrL(CO)_2$ provide the first examples of stable low valent 2nd and 3rd row Group VIII metal complexes with BAII ligands. As this work demonstrates, the easily modified ligand may offer opportunities for tuning electronically the chemistry at the metal center without altering the geometry or steric considerations of the coordination sphere.

Current studies are focused on assessing the effects of remote substituents on the BAII ligand on the chemistry of the metal center.

Acknowledgement

Encouragement from and very stimulating discussions with Dr. Lee R. Mahoney are gratefully acknowledged.

References

1 J.A. Elvidge and R.P. Linstead, J. Chem. Soc., (1952) 5000.
2 M.A. Robinson, S.I. Trotz and T.J. Hurley, Inorg. Chem., 6 (1967) 392.
3 W.O. Siegl, Inorg. Nucl. Chem. Letters, 10 (1974) 825.
4 Cf. R.D. Gillard, K. Harrison and I.H. Mather, J. Chem. Soc. Dalton, (1975) 133.
5 S. Trofimenko, Accounts Chem. Res., 4 (1971) 17; Chem. Rev., 72 (1972) 497.
6 P.F. Clark, J.A. Elvidge and R.P. Linstead, J. Chem. Soc., (1953) 3593.
7 Ref. 3 and this work.
8 W.O. Siegl, S.J. Lapporte and J.P. Collman, Inorg. Chem., 10 (1971) 2158.