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in conjunction with
THE NATIONAL RESEARCH COUNCIL OF CANADA
and
THE CHEMICAL INSTITUTE OF CANADA

COORDINATION CHEMISTRY — XIV

(TORONTO, 1972)

Plenary Lectures

Symposium Editor
A. B. P. LEVER



Plenary lectures presented at the

**XIVth INTERNATIONAL CONFERENCE ON
COORDINATION CHEMISTRY**

Conférences plénières présentées à la

**XIVe CONFERENCE INTERNATIONALE SUR
LA CHIMIE DE COORDINATION**

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et
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CHIMIE DE COORDINATION—XIV

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XIV^e CONFERENCE INTERNATIONALE SUR
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à Toronto, Canada
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Rédacteur du Symposium
A. B. P. LEVER
Université de York, Ontario

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SYNTHESIS AND PROPERTIES OF TRANSITION METAL TO CARBON BONDS

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ABSTRACT

The known properties of alkyl and aryl derivatives of transition elements are reviewed, with particular attention to binary compounds of this type. Factors contributing to thermal stability of metal-carbon σ -bonds are discussed and new contributions are presented dealing with: (i) chemistry of titanium(IV) and titanium(II); (ii) metal-carbon bonds in *N,N'*-ethylenebis(salicylideneiminato) complexes of iron and cobalt; (iii) reactivity of rhenium(I) bromo-carbonyl complexes; (iv) use of metal carbonyls as a source of zerovalent metals in the preparations of binary complexes of 9,10-phenanthrenequinone and (v) synthesis of cyclopentadienyl-alkyl and cyclopentadienyl-aryl derivatives of uranium(IV).

INTRODUCTION

In the past decades chemists have lived in the belief that alkyl and aryl derivatives of transition metals had to be unstable. This belief came from the observation that while several organometallic compounds of non-transition elements were known and were thermally stable under ordinary conditions, pure binary compounds of transition elements had been until quite recently a rarity. Some of them have been recently synthesized, however (see *Table 1*). Some examples of non-binary alkyl and aryl derivatives of transition metals are given in *Tables 2* and *3*. Although the *Tables* contain only a limited number of selected examples, some interesting observations can be made.

Table 1. Some binary alkyl derivatives of d-transition elements

| Compound | Colour | m.p. (°C) | Reference |
|-----------------------------------------------------------------|-------------|--------------------|-----------|
| Ti(CH ₂ C ₆ H ₅) ₄ | red-brown | 70–71 | 1 |
| Zr(CH ₂ C ₆ H ₅) ₄ | yellow | 133–134 | 1 |
| Cr(CH ₂ SiMe ₃) ₄ | dark-purple | 38 | 2a, 2b |
| WMe ₆ | red | c. 30 (dec. 50) | 3 |

(i) Stable organometallic compounds of transition metals exist even with

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Table 2. Some non-binary alkyl and aryl compounds of d-transition elements in their highest usual oxidation states

| Compound | Colour | m.p. (°C) | Reference |
|---------------------------------------------------------------------------------------------------------------|------------|--------------|--------------|
| Ti(C ₅ H ₅) ₂ (CH ₂ C ₆ H ₅) ₂ | violet | 109–111 | 4a, 4b |
| Zr(C ₅ H ₅) ₂ (CH ₂ C ₆ H ₅) ₂ | yellow | c. 100 | 5 |
| Zr(C ₅ H ₅) ₂ Me ₂ | — | — | 6 |
| VO(CH ₂ SiMe ₃) ₃ | yellow | 75 | 2 |
| FeSaEn-CH ₂ C ₆ H ₅ † | red | dec. 70 | 7 |
| CoSaEn-Me | red | — | 8, 9, 10, 11 |
| Ni(lipy)Me ₂ | green | — | 12a, 12b |
| Pt(PR ₃) ₂ Me ₄ | colourless | — | 13a |
| Pt(C ₅ H ₅)Me ₃ | colourless | 108.5‡ | 13b |
| Au ₂ Me ₆ (NH ₂ CH ₂ CH ₂ NH ₂) | colourless | dec. 94–98 | 14a |
| Au(PMe ₃)Me ₃ | — | dec. 120 | 14b, 15 |
| Au(PPh ₃)(C ₆ F ₅) ₃ | colourless | dec. 243–246 | 16 |

† FeSaEn stands for : *N,N'*-ethylenebis(salicylideneiminato)iron(II).

‡ At 115°C, about 99 per cent of the substance was recovered unchanged after 75 min.

the metal in its highest usual oxidation state (Ti^{IV}, Zr^{IV}, V^V, W^{VI}, Fe^{III}, Pt^{IV}, Au^{III}).

(ii) Alkyl- and aryl-metal bonds can be stable also when the metal is in an unusually low oxidation state (Mo^{II}, Re^I, Os^{II}, Co^I): this usually happens in connection with cyclopentadienyl and carbon monoxide groups, especially the latter, which are known to stabilize low oxidation states as π -acids.

Before discussing points (i) and (ii) in some detail, it is worthwhile to define what should usually be meant by stability of metal-carbon σ -bonds.

These introductory remarks are essentially restricted to metal-alkyl and metal-aryl σ -bonds, whereas the rest of this article will deal with metal-carbon bonds in general, including two-electron carbon donors, such as carbon monoxide and isocyanides.

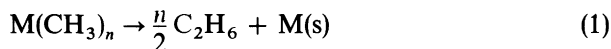
Thermodynamic stability should be distinctly separated from kinetic stability, of course. Unfortunately, sufficient data are not yet available to discuss thermodynamic stability properly. It seems, however, from the few data available (see Table 4) that metal-carbon σ -bonds to titanium and platinum are not inherently weak, since the estimated values for the mean dissociation energies range from 60 to 84 kcal mol⁻¹. This does not necessarily mean that the observed thermal stability of some metal-carbon bonds to

Table 3. Some non-binary alkyl compounds of d-transition elements in low oxidation states

| Compound | Colour | m.p. (°C) | Reference |
|------------------------------------------------------------------------|------------|-----------|-----------|
| Cr(C ₅ H ₅)(CO) ₃ Me | yellow | — | 17 |
| Cr(C ₆ H ₅ Me ₃) ₂ · 3THF | violet | dec. 50 | 18 |
| Mo(C ₅ H ₅)(CO) ₃ Et | yellow | 77–78 | 17 |
| Mn(CO) ₅ Me | colourless | 94.5–95 | 19 |
| Re(CO) ₅ Me | colourless | 120 | 20 |
| Os(CO) ₄ Me ₂ | colourless | — | 21, 22 |
| Co(CO) ₄ Me | yellow | –44 | 23 |

SYNTHESIS AND PROPERTIES OF TRANSITION METAL TO CARBON BONDS

transition metals is thermodynamic. In fact, it is highly probable that most or all of the compounds containing, for example, metal-methyl bonds would be thermodynamically unstable with respect to the homolytic fission:



Most of the compounds reported in *Tables 1* and *2* have been prepared quite recently. While some years ago it appeared necessary to find an explanation for the stabilizing effect of ligands such as carbon monoxide and tertiary phosphines, the inherent instability of metal-carbon bonds being taken for granted, today it is important to interpret correctly the experimental observation that some binary metal-alkyl compounds can be isolated and handled under normal operative conditions.

The situation could therefore be stated in the following terms. The problem concerning the existence of thermally-stable transition-element-carbon bonds is less intriguing now than it was some years ago. However, the thermal stability, which is controlled almost certainly by kinetic factors, has still to be explained. The main factors which have been or may be considered in order to explain the scarce availability of low-energy paths for the breaking of metal-carbon σ -bonds are: (i) stabilization of metal-carbon bonds with respect to olefin elimination^{2b, 3}; (ii) the electronic configuration and the

Table 4. Calorimetric mean bond dissociation energies (MBDE) of some metal-carbon bonds

| Metal-C bond | Compound | MBDE (kcal mol ⁻¹) | Reference |
|--------------|-----------------------------------------------------------------|-----------------------------------|-----------|
| Ti-Me | Ti(C ₅ H ₅) ₂ Me ₂ | 60 | 24 |
| Ti-Ph | Ti(C ₅ H ₅) ₂ Ph ₂ | 84 | 24 |
| Pt-Ph | Pt(PEt ₃) ₂ Ph ₂ | 60 | 25 |
| Hg-Me | HgMe ₂ | 29 | 26 |

symmetry of the central metal atom, which in some cases can prevent the mixing of ground and excited vibrational states²⁷; (iii) the promotion of electrons to excited states²⁸, which may explain the photochemical lability of surprisingly stable metal-carbon bonds of some cobalt(III) derivatives⁸⁻¹¹; (iv) the absence of vacant coordination positions and (v) a relatively high oxidation state for the central metal atom.

Point (v) originates from the data of *Tables 1* and *2* and may be related, in classical terms, to an increased stability of the carbanion bonded to the metal. Of course, it is very likely that none of the above mentioned factors alone will explain all the known facts.

That the metal has to be saturated from a coordinative point of view (this may be either a kinetic or a thermodynamic stabilization) should be an important fact.

It is interesting to note that tetrabenzyltitanium(IV) has an intense red-brown colour, which is certainly not to be attributed to a d→d transition in view of the high intensity and, of course, to the fact that we are dealing with a

d^0 -system. The intensity of the absorption is in favour of a charge-transfer type of transition. It is interesting to observe that the x-ray structure of this compound^{29, 30} has clearly shown that, in spite of the fact that there is not a π -allyl type of stabilization to be invoked, involving two of the aromatic ring carbon atoms, the conformation of the molecule is such that a considerable interaction may be suggested between the central metal atom and at least one of the aromatic groups. As it can be seen in *Figure 1*, one of the four Ti-C-C

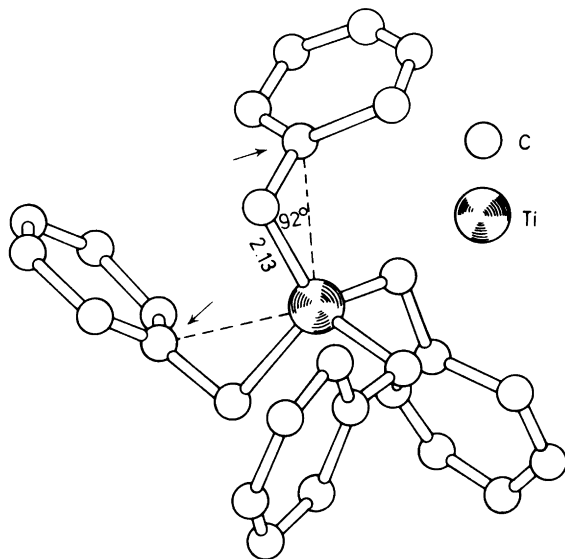


Figure 1. Molecular structure of $\text{Ti}(\text{CH}_2\text{C}_6\text{H}_5)_4$ showing that the angle at one of the four methylene groups is 92° . From G. R. Davies, J. A. J. Jarvis and B. T. Kilbourn, *Chem. Commun.*, 1511 (1971). See also Ref. 29

angles at the methylene group is 92° . The other such angles are 98° , 109° and 115° , two of them, therefore, being much smaller than expected. An interaction between empty d-orbitals of the metals and p-orbitals of the aromatic rings was therefore suggested^{29, 30}. It is possible that this interaction may at least in part be responsible for both the stability (occupation of coordination sites) and the colour of the complex. In the similar zirconium compound³¹, $\text{Zr}(\text{CH}_2\text{C}_6\text{H}_5)_4$, the angles at the methylene groups are 85° , 90° , 92° and 101° , i.e. even smaller than for the titanium compound.

In connection with colour, it should be mentioned that the reported³ red colour of hexamethyltungsten(VI) is intriguing since it is not obvious which orbitals are involved in the electronic transitions occurring at such low energy.

We can now consider some of the experimental results that have been recently obtained in our and other laboratories. Some of these results may be helpful towards a better understanding of the problem connected with the stability of metal-carbon σ -bonds. The metals at the beginning (titanium