TABLE I

N.M.R. SPECTRUM OF C-4 PROTON OF Δ⁴-3-KETOSTEROIDS

| | Substituent at C-6 | Average δ (c.p.s.)[7] | Average line width (c.p.s.)[8] | No. of compounds |
|---|---|---|---|---|
| | None | 344.2 | 3.4 | 6 |
| | 6β-D | 343.5 | 2.3 | 3 |
| 10-Methyl | 6β-CH₃ | 344.3 | 2.3 | 3 |
| | 6β-Br | 355.0 | 2.4 | 1 |
| | 6α-Br | 390.6 | $J = 2.0$ | 1 |
| | 6α-CH₃ | 347.4 | $J = 1.7$ | 4 |
| 10-H | None | 350.0 | 4.3 | 4 |
| (19-Nor) | 6β-CH₃ | 353.5 | $J = 2.0$ | 1 |

which almost certainly is due to C-4, 10β proton–proton coupling.

The appearance of the C-4 proton as a broadened peak when two protons are present at C-6 but as a sharp doublet in the presence of a 6α-substituent may be rationalized by a first-order treatment[11] of the C-4 and two C-6 protons as an ABX system which indicates that two of the possible six lines are of near zero intensity while the remaining four are so closely spaced as to be unresolved by the present instrument and appear as a broadened signal. When the 6α-proton is replaced by halogen or methyl the system under consideration reduces to the AX type in which the X portion consists of only two lines.

(11) Cf. J. D. Roberts, "An Introduction to the Analysis of Spin–Spin Splitting in High-Resolution Nuclear Magnetic Resonance Spectra," W. A. Benjamin, Inc., New York, N. Y., 1961, p. 71.

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LINKAGE ISOMERISM: SYNTHESIS OF THIOCYANATO
AND ISOTHIOCYANATO ISOMERS OF SOME
PALLADIUM(II) COMPLEXES

Sir:

The first example of linkage isomerism for metal complexes was reported in 1893 by Jørgensen[1] for nitro (Co–NO₂) and nitrito (Co–ONO) ammines of cobalt-(III). Recently, it was possible to extend this type of isomerism to include complexes of rhodium(III), iridium(III) and platinum(IV).[2] These have been the only examples of linkage isomers in metal complexes.

The thiocyanate ion is often suggested as an example of another ligand that might possibly be used to produce linkage isomers. Typical of textbook statements is the following: "the thiocyanate ion coordinates through sulfur in some complexes and through nitrogen in others but no isomeric pair has as yet been found".[3]

We wish to report the synthesis of thiocyanato (Pd–SCN) and isothiocyanato (Pd–NCS) isomers of some palladium(II) complexes. The method used is based on the interesting and significant observation made by Turco and Pecile.[4] They found that, for Pd(II) and Pt(II) complexes, coördinated thiocyanate ion is either S- or N-bonded, depending on the nature of the other ligands present. Thus, the systems [M(SCN)₄]⁻² and [M(NH₃)₂(SCN)₂] are S-bonded, whereas [M(PR₃)₂(NCS)₂] is N-bonded. It follows that in these systems there should be some borderline ligands for which the energy difference between the M–SCN and M–NCS isomers is small. Triphenylarsine, Ph₃As, was found to be such a ligand. Using this ligand it is possible to obtain the unstable kinetic product before it rearranges to the stable isomer (1).

(1) S. M. Jørgensen, Z. anorg. allgem. Chem., 5, 169 (1893).
(2) F. Basolo and G. S. Hammaker, J. Am. Chem. Soc., 82, 1001 (1960); Inorg. Chem., 1, 1 (1962).
(3) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1962, p. 538.
(4) A. Turco and C. Pecile, Nature, 191, 66 (1961).
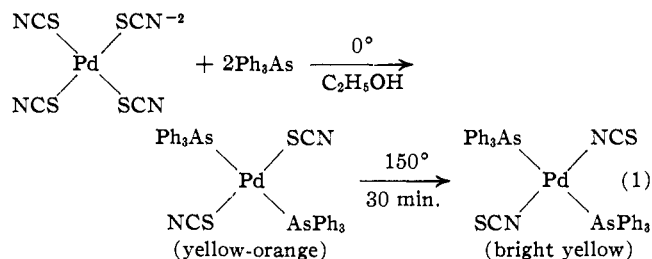


In a typical preparation, 1.03 g. (2.47 mmoles) of K₂Pd(SCN)₄, dissolved in 25 cc. of absolute ethanol and 5 drops of water, and 1.52 g. (4.95 mmoles) of triphenylarsine, dissolved in 25 cc. of absolute ethanol and 5 drops of ethyl ether, were cooled to 0°, then mixed in a vessel surrounded by an ice bath. After stirring for 1 min., the yellow-orange S-bonded product was precipitated by the addition of 50 cc. of ice water, isolated, washed with ice-cold ethanol and ethyl ether and dried in a vacuum desiccator over P₂O₅ (yield, 1.87 g. or 91%).

Anal. Calcd. for [Pd(AsPh₃)₂(SCN)₂]: C, 54.7; H, 3.6; N, 3.4. Found, before heating: C, 54.5; H, 3.8; N, 3.3; after heating: C, 55.0; H, 3.8; N, 3.6.

The S-bonded isomer is stable at room temperature in the solid state for weeks but rearranges readily at elevated temperatures and in solution it immediately gives the N-bonded form. Because of the possible complication due to the chance of concurrent geometric isomerism, it was necessary to prepare a system containing a bidentate ligand. This was accomplished using 2,2'-bipyridine, bipy, at the temperature of a Dry Ice–acetone mixture (2).
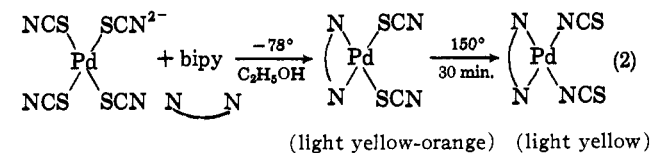


When alcoholic solutions of equimolar quantities of K₂Pd(SCN)₄ and 2,2'-bipyridine, pre-cooled to −78°, were mixed in a reaction vessel surrounded by a Dry Ice–acetone bath, no formation of solid took place. The solution was removed from the bath and, after about 10 min., had become opaque. An unidentified orange solid was removed by filtration and the desired S-bonded isomer immediately separated in the filtrate. This was isolated, washed with −78° ethanol and ethyl ether and dried in a vacuum desiccator over Mg-(ClO₄)₂.

Anal. Calcd. for [Pd(bipy)(SCN)₂]: C, 38.0; H, 2.1; N, 14.8. Found, before heating: C, 38.2; H, 2.5; N, 15.0; after heating: C, 38.5; H, 2.4; N, 14.8.

The nature of the thiocyanate bonding in these two sets of isomers was determined by examining the infrared spectra of Nujol mulls of the solid compounds. It has been shown[4,5] that the C–S stretching vibrations of coördinated thiocyanates fall into two ranges: M–SCN, 690–720 cm.⁻¹; M–NCS, 780–860 cm.⁻¹. The C–S stretching frequencies found were [Pd(AsPh₃)₂(SCN)₂], blank in M–NCS range, obscured by phenyl absorption in M–SCN range; [Pd(AsPh₃)₂(NCS)₂], 854 cm.⁻¹; [Pd(bipy)(SCN)₂], 700 cm.⁻¹; [Pd(bipy)-(NCS)₂], 842 cm.⁻¹.

Under high resolution, the frequencies of the C–N stretching vibrations were also observed to vary, in accordance with the order predicted by Mitchell and Wil-

(5) M. M. Chamberlain and J. C. Bailar, Jr., J. Am. Chem. Soc., 81, 6412 (1959); J. Lewis, R. S. Nyholm and P. W. Smith, J. Chem. Soc., 4590 (1961).

liams,[6] *i.e.*, M–SCN $\gg$ M–NCS, as follows: [Pd(As-Ph₃)₂(SCN)₂], 2119 cm.$^{-1}$; [Pd(AsPh₃)₂(NCS)₂], 2089 cm.$^{-1}$; [Pd(bipy)(SCN)₂], 2117 and 2108 cm.$^{-1}$ (doublet); [Pd(bipy)(NCS)₂], 2100 cm.$^{-1}$.

Conductivity measurements were made in dimethylformamide at 25° and a concentration of $10^{-3}$ $M$. The molar conductances (ohm$^{-1}$ cm.$^{-2}$ mole$^{-1}$) obtained fall within the range of conductance exhibited by non-electrolytes in DMF as found by Quagliano, *et al.*[7]: [Pd-(AsPh₃)₂(SCN)₂], 13.3; [Pd(AsPh₃)₂(NCS)₂], 13.8; [Pd-(bipy)(SCN)₂], 20.3; [Pd(bipy)(NCS)₂], 20.8.

That the S-bonded 2,2'-bipyridine product is the designated isomer and not [Pd(bipy)₂][Pd(SCN)₄] was proven by preparing this pink Magnus-type salt and showing that it differs from the thiocyanato isomer. Here then is an unequivocal example of thiocyanato-*iso*thiocyanato isomerism in metal complexes.[8] Research will be done on the kinetics and mechanism of isomerization in these and other systems. Work is now in progress on the synthesis of the analogous linkage isomers of the type M–SeCN and M–NCSe and possibly M–NCO and M–OCN.

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(6) P. C. H Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 1912 (1960).

(7) J. V. Quagliano, J. Fujita, G. Franz, D. J. Phillips, J. A. Walmsley and S. Y. Tyree, *J. Am. Chem. Soc.*, **83**, 3770 (1961).

(8) Just as there are borderline ligands in determining the nature of thiocyanate ion bonding in metal complexes, there must also be borderline metals. Cadmium(II) is such a metal ion. In aqueous solution, the system Cd(II)–CNS⁻ shows Cd–NCS and Cd–SCN species. Under the same conditions, the other two members of this triad show only Zn–NCS and Hg(II)–SCN species, respectively. These observations were made independently by R. A. Plane, using Raman spectra, and by O. W. Howarth R. E. Richards and L. M. Venanzi, using n.m.r. (private communication).

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## ADDITIVITY RELATIONSHIPS IN CARBON-13 CHEMICAL SHIFT DATA FOR THE LINEAR ALKANES[1]

*Sir:*

Carbon-13 chemical shift data obtained in this laboratory on the linear alkanes are presented in Table I along with values obtained by Spiesecke and Schneider[2] for methane and ethane. The unfavorable sensitivity in detecting the carbon-13 nuclei in natural abundance (1.1%) was overcome by simultaneously irradiating the associated protons in a double resonance experiment. Spin decoupling in this manner results in a sizable signal enhancement which is due to multiplet collapse and a nuclear Overhauser effect. By accurately measuring the two irradiating frequencies when the proton decoupler has been adjusted to give a maximum signal, it is possible to determine the chemical shift with an accuracy of ±1 c.p.s. (±0.07 p.p.m.). All chemical shift data are given relative to benzene.

Application of the method of least squares to the data for butane through decane gave additive substituent parameters for the nine linear alkyl radicals, methyl through nonyl, and for the chemical shift of methane. The linear mathematical expression used in the treatment is

$$\delta(C_j) = \delta(CH_4) + \sum_i n_{ij}\delta(R_i) \tag{1}$$

where $\delta(CH_4)$ and $\delta(C_j)$ are the chemical shifts of methane and of the $j^{th}$ carbon, respectively. In

addition, $n_{ij}$ is the number of $R_i$ radicals attached to the $j^{th}$ carbon, and $\delta(R_i)$ is the additive chemical shift parameter assigned to the $R_i$ radical. The chemical shift data on methane through propane were not included in the least squares treatment because of the larger intrinsic error in the recorded values. The data in ref. 2 were reported to have an error of ±0.3 p.p.m. and our values on propane have a similar error due to the inability to resolve the two resonance signals in the decoupling experiment. The standard deviation of the fit for the more precise data on butane through decane is 0.081 p.p.m., a value which corresponds directly with the experimental error in these data. Therefore, within experimental error all the data of Table I can be said to follow the additivity relationship proposed in Table II.

TABLE I

CARBON-13 CHEMICAL SHIFT DATA FOR THE LINEAR ALKANES

| Compound | | Exptl. value | Calcd. value | Deviation |
|---|---|---|---|---|
| Methane (ref. 2) | C₁ | 130.8 ± 0.3 | 131.47 | +0.67 |
| Ethane (ref. 2) | C₁ | 122.8 ± 0.3 | 122.37 | − .43 |
| Propane | C₁ | 113.3 ± 0.3 | 112.92 | − .38 |
| | C₂ | 112.9 ± 0.3 | 113.27 | + .37 |
| Butane | C₁ | 115.67 | 115.49 | − .18 |
| | C₂ | 103.87 | 103.82 | − .05 |
| Pentane | C₁ | 115.15 | 115.12 | − .03 |
| | C₂ | 106.32 | 106.39 | + .07 |
| | C₃ | 94.35 | 94.37 | + .02 |
| Hexane | C₁ | 115.00 | 115.02 | + .02 |
| | C₂ | 105.97 | 106.02 | + .05 |
| | C₃ | 96.85 | 96.94 | + .09 |
| Heptane | C₁ | 114.93 | 114.97 | + .04 |
| | C₂ | 105.89 | 105.92 | + .03 |
| | C₃ | 96.49 | 96.57 | + .08 |
| | C₄ | 99.42 | 99.51 | + .09 |
| Octane | C₁ | 114.83 | 114.92 | + .09 |
| | C₂ | 105.86 | 105.87 | + .01 |
| | C₃ | 96.51 | 96.47 | − .04 |
| | C₄ | 99.21 | 99.14 | − .07 |
| Nonane | C₁ | 114.86 | 114.94 | + .08 |
| | C₂ | 105.81 | 105.82 | + .01 |
| | C₃ | 96.44 | 96.42 | − .02 |
| | C₄ | 99.04 | 99.04 | 0 |
| | C₅ | 98.77 | 98.77 | 0 |
| Decane | C₁ | 114.86 | 114.86 | 0 |
| | C₂ | 105.91 | 105.84 | − .07 |
| | C₃ | 96.46 | 96.37 | − .09 |
| | C₄ | 99.02 | 98.99 | − .03 |
| | C₅ | 98.64 | 98.67 | + .03 |

TABLE II

ADDITIVE CHEMICAL SHIFT PARAMETERS

| Groups | Chemical shifts in p.p.m. |
|---|---|
| Methane | 131.47 (rel. to C₆H₆) |
| Radicals | |
| Methyl | − 9.10 |
| Ethyl | −18.55 |
| Propyl | −15.98 |
| Butyl | −16.35 |
| Pentyl | −16.45 |
| Hexyl | −16.50 |
| Heptyl | −16.55 |
| Octyl | −16.53 |
| Nonyl | −16.61 |

As the substituent corrections in Table II are terms which shift the resonances to lower fields, a paramagnetic shift such as proposed by McConnell[3] and Pople[4] is a possible explanation. Interactions of this type due

(3) H. M. McConnell, *ibid.*, **27**, 226 (1957).

(4) J. A. Pople, *Proc. Roy. Soc.* (London), **A239**, 550 (1957).