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Reaction of Tetracyanoethylene with the Thiolato-Bridged d^8 Diiridium Complexes [Ir(μ-S-*t*-Bu)(CO)(PR$_3$)]$_2$, R = Me, Ph, and OMe. Crystal Structure of the Complex [Ir(μ-S-*t*-Bu)(CO)(P(OMe)$_3$)]$_2$[C(CN)$_2$]$_2$

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A series of thiolato-bridged dinuclear d^8 iridium complexes [Ir(μ-S-*t*-Bu)(CO)(PR$_3$)]$_2$ with R = Me, Ph, or OMe reacts with tetracyanoethylene to yield quantitatively 1/1 adducts. The complex [Ir(μ -S-*t*-Bu)(CO)(P(OMe)$_3$)]$_2$[C(CN)$_2$]$_2$ has been characterized crystallographically. The compound crystallizes with two molecules in a cell whose dimensions are a = 11.867 (1) Å, b = 15.988 (1) Å, c = 10.456 (1) Å, α = 108.79 (2)°, β = 113.33 (2)°, and γ = 72.00 (2)°. On the basis of 2726 unique reflections with $F_o^2 \geq 3\sigma(F_o^2)$, the structure was refined by full-matrix least-squares techniques to conventional agreement indices of $R(F)$ = 0.026 and $R_w(F)$ = 0.029. The environments of the two iridium atoms are markedly different. One is attached to one terminal carbonyl, two phosphites, and two bridging *tert*-butyl thiolato ligands and the other is attached to one terminal carbonyl and a π-bonded (CN)$_2$CC(CN)$_2$ group. A distance of 2.679 (1) Å between the two iridium atoms, together with infrared information, indicates the presence of a coordinate covalent Ir–Ir bond.

Introduction

Recent studies from our laboratory have been concerned with the synthesis[1] and the reactivity of "hinge-shaped"[2] double-square-planar thiolato-bridged diiridium(I) complexes toward activated alkynes[3] and molecular hydrogen.[4] As part of the continuing interest in the study of oxidative addition of small molecules on these diiridium compounds, we initiated an investigation of the reaction of tetracyanoethylene with [Ir(μ-S-*t*-Bu)(CO)(PR$_3$)]$_2$ (R = Me, Ph, OMe) compounds. In this paper, we report the synthesis and the structural characterization of unusual dinuclear tetracyanoethylene adducts of the general formula [Ir(μ-S-*t*-Bu)(CO)(PR$_3$)]$_2$[C-(CN)$_2$]$_2$.

Experimental Section

All reactions were carried out under a dry and oxygen-free dinitrogen atmosphere. Microanalyses were performed by the Service Central de Microanalyses du CNRS. Infrared spectra were recorded in dichloromethane solutions or cesium bromide dispersions, by using a Perkin-Elmer 225 spectrometer. In the ν(CO) region, the spectra were calibrated by water vapor lines. ^{1}H NMR spectra were obtained at 60 MHz on a Varian A60A spectrometer. Chemical shifts were measured with respect to internal Me$_4$Si and are reported on the τ scale. Proton-noise-decoupled ^{31}P NMR spectra were performed at 36.4 MHz on a Bruker WH90 spectrometer. Chemical shifts were measured with respect to external H$_3$PO$_4$ and are given in ppm downfield positive.

Preparation of Complexes. [Ir(μ-S-*t*-Bu)(CO)(PR$_3$)]$_2$ complexes were prepared as previously described.[1]

Preparation of [Ir(μ-S-*t*-Bu)(CO)(P(OMe)$_3$)]$_2$(C(CN)$_2$)$_2$. The iridium(I) complex [Ir(μ-S-*t*-Bu)(CO)(P(OMe)$_3$)]$_2$ (0.300 g) was dissolved in dichloromethane (8 mL) and a dichloromethane solution of tetracyanoethylene (0.044 g) was added in an equimolar amount, at room temperature. The mixture was stirred, and within a few minutes, the solution changed from red orange to brown. When the dichloromethane solution was concentrated, the title complex was obtained as brown orange crystals (0.270 g, 78%).

Anal. Calcd for C$_{22}$H$_{36}$N$_4$Ir$_2$O$_8$P$_2$S$_2$: C, 26.55; H, 3.65; N, 5.63; S, 6.44. Found: C, 26.62; H, 3.62; N, 5.86; S, 6.27.

Preparation of [Ir(μ-S-*t*-Bu)(CO)(PMe$_3$)]$_2$(C(CN)$_2$)$_2$. This compound was prepared similarly with comparable yield.

(1) (a) J.-J. Bonnet, J. Galy, D. de Montauzon, and R. Poilblanc, *J. Chem. Soc., Chem. Commun.,* 47 (1977); (b) D. de Montauzon, P. Kalck, and R. Poilblanc, *J. Organomet. Chem.,* in press.
(2) R. Poilblanc, *J. Organomet. Chem.,* **94,** 241 (1975).
(3) J. Devillers, J.-J. Bonnet, D. de Montauzon, J. Galy, and R. Poilblanc, *Inorg. Chem.,* in press.
(4) (a) A. Thorez, A. Maisonnat, and R. Poilblanc, *J. Chem. Soc., Chem. Commun.,* 518 (1977); (b) J.-J. Bonnet, A. Thorez, A. Maisonnat, J. Galy, and R. Poilblanc, *J. Am. Chem. Soc.,* **101,** 5940 (1979).

Table I. Summary of Crystal Data and Intensity Collection

compd	[Ir(μ-S-*t*-Bu)(CO)(P(OMe)$_3$)]$_2$-[C(CN)$_2$]$_2$
formula	C$_{22}$H$_{36}$N$_4$O$_8$P$_2$S$_2$Ir$_2$
fw	995.03
cell parameters	a = 11.867 (1) Å
	b = 15.988 (1) Å
	c = 10.456 (1) Å
	α = 108.79 (2)°
	β = 113.33 (2)°
	γ = 72.00 (2)°
V	1686.5 Å^3
Z	2
d(calcd)	1.959 g·cm^{-3}
d(measd in aq ZnCl$_2$)	1.90 g·cm^{-3}
space group	$P\bar{1}$
cryst dimens	0.165 × 0.120 × 0.277 × 0.227
boundary faces of the prism	{11$\bar{1}$, 0$\bar{1}$1, 01$\bar{1}$, 1$\bar{1}$1}
temp	20 °C
radiation	Mo Kα (0.7093 Å) from monochromator
linear abs factor	22.386 cm^{-1} (Mo Kα)
transmission factors[17]	0.598–0.745
takeoff angle	3.5°
scan speed	2° in 2θ/min
scan range	0.65° below Kα$_1$ to 0.65° above Kα$_2$
bkgd counts	20 s
2θ limits	3–46°
final no. of variables	362
unique data used	2726, $F_o^2 > 3\sigma(F_o^2)$
quantity minimized	$\Sigma w(|F_o| - |F_c|)^2$
wt	$w = 4F_o^2/\sigma^2(F_o^2)$
$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$	0.026
$R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2)^{1/2}$	0.029
std error in observn of unit wt	0.92 e

Anal. Calcd for C$_{22}$H$_{36}$N$_4$Ir$_2$O$_2$P$_2$S$_2$: C, 29.39; H, 4.04; N, 6.23; S, 7.13. Found: C, 29.88; H, 4.01; N, 6.15; S, 6.57.

Preparation of [Ir(μ-S-*t*-Bu)(CO)(PPh$_3$)]$_2$(C(CN)$_2$)$_2$. The mixture of [Ir(μ-S-*t*-Bu)(CO)(PPh$_3$)]$_2$ and TCNE in CH$_2$Cl$_2$ was stirred, and within a few minutes, complete precipitation of the product occurred. The yellow solid was washed with toluene and hexane.

Anal. Calcd for C$_{52}$H$_{48}$N$_4$Ir$_2$O$_2$P$_2$S$_2$: C, 49.12; H, 3.81; S, 5.04. Found: C, 49.42; H, 3.90; S, 4.80.

X-ray Study. Examination of crystals of [Ir(μ-S-*t*-Bu)(CO)(P-(OMe)$_3$)]$_2$ by precession and Weissenberg methods using Mo Kα radiation failed to reveal the presence of any symmetry elements other than the center of symmetry imposed by Friedel's law. Cell constants, determined in the manner described below, are given in Table I. On the basis of a calculated volume of 1686.6 Å^3 and two formula units in the cell, the calculated density of 1.959 g·cm^{-3} and the density of 1.90 (1) g·cm^{-3} observed by flotation in aqueous ZnCl$_2$ are in good

Table II. Positional and Thermal Parameters for the Atoms of $[Ir(\mu\text{-S-}t\text{-Bu})(CO)(P(OMe)_3)]_2[C(CN)_2]_2$

atom	x^a	y	z	$\beta_{11}{}^b$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ir(1)	-0.22448 (5)	0.21094 (4)	0.14396 (6)	5.70 (4)	3.30 (4)	8.59 (11)	-0.56 (4)	2.28 (7)	1.15 (5)
Ir(2)	0.00121 (6)	0.24876 (4)	0.30810 (6)	5.67 (8)	3.67 (4)	8.67 (11)	-0.51 (5)	1.99 (8)	1.28 (5)
P(1)	-0.2563 (4)	0.1005 (3)	0.2076 (4)	7.6 (4)	4.4 (2)	14.2 (7)	-0.6 (3)	3.9 (5)	2.2 (3)
P(2)	-0.4329 (4)	0.2556 (3)	0.0181 (5)	6.5 (4)	5.3 (3)	13.2 (6)	-0.6 (3)	1.2 (5)	2.0 (3)
S(1)	-0.1718 (3)	0.2824 (2)	0.3924 (4)	7.2 (4)	4.0 (2)	8.9 (5)	0.0 (2)	3.2 (4)	1.8 (3)
S(2)	-0.1518 (3)	0.3392 (2)	0.1536 (4)	7.8 (4)	3.4 (2)	9.5 (5)	-0.3 (2)	3.7 (4)	1.7 (3)
O(1)	-0.1395 (11)	0.0686 (7)	-0.0895 (12)	16.8 (17)	5.7 (7)	16.2 (19)	-2.6 (9)	9.7 (15)	-2.3 (9)
O(2)	0.1479 (11)	0.1378 (7)	0.1130 (12)	14.5 (16)	7.6 (8)	19.3 (21)	1.4 (9)	10.9 (16)	0.1 (10)
O(3)	-0.1459 (9)	0.0504 (6)	0.3188 (10)	11.9 (13)	4.7 (6)	16.0 (17)	0.0 (7)	4.7 (13)	4.6 (8)
O(4)	-0.2997 (9)	0.0239 (6)	0.0705 (11)	11.7 (13)	5.3 (6)	17.5 (18)	3.0 (7)	5.4 (13)	1.3 (9)
O(5)	-0.3640 (9)	0.1312 (7)	0.2774 (13)	11.4 (14)	5.9 (7)	27.2 (23)	-0.2 (8)	11.4 (15)	3.6 (10)
O(6)	-0.4445 (10)	0.3289 (8)	-0.0559 (12)	10.0 (14)	9.6 (9)	22.2 (22)	-3.0 (9)	-3.9 (14)	9.2 (12)
O(7)	-0.5049 (9)	0.1828 (7)	-0.1005 (12)	8.7 (13)	8.4 (8)	18.3 (20)	-3.2 (8)	-2.8 (13)	2.9 (11)
O(8)	-0.5235 (10)	0.2981 (8)	0.1104 (12)	8.2 (13)	11.6 (10)	21.8 (22)	-0.3 (9)	4.5 (15)	-0.9 (11)
N(1)	0.1326 (14)	0.4164 (11)	0.7025 (17)	12.7 (20)	10.0 (12)	22 (3)	-3.1 (12)	4.4 (20)	-8.2 (15)
N(2)	0.3500 (14)	0.2868 (11)	0.4218 (17)	10.7 (20)	12.5 (14)	26 (3)	-4.1 (14)	7.6 (22)	1.5 (16)
N(3)	0.0807 (15)	0.1902 (11)	0.6884 (16)	19.7 (24)	10.7 (12)	20.3 (29)	2.0 (13)	9.5 (22)	8.4 (16)
N(4)	0.3055 (13)	0.0551 (9)	0.4235 (15)	10.9 (18)	6.9 (10)	19.1 (25)	2.0 (11)	3.2 (17)	1.6 (13)
C(1)	-0.1736 (15)	0.1251 (10)	-0.0061 (17)	12.6 (22)	4.4 (10)	11.1 (25)	-4.1 (12)	1.5 (19)	1.8 (12)
C(2)	0.0951 (14)	0.1813 (10)	0.1892 (17)	7.8 (18)	4.7 (10)	13.8 (26)	-0.1 (11)	4.9 (18)	-0.0 (12)
C(3)	0.1581 (13)	0.2877 (10)	0.4857 (16)	6.7 (17)	5.5 (10)	13.8 (25)	-2.0 (11)	3.3 (17)	0.6 (13)
C(4)	0.1395 (13)	0.1966 (10)	0.4799 (15)	6.9 (17)	4.4 (9)	10.9 (22)	0.3 (10)	3.9 (16)	1.8 (11)
C(5)	0.1419 (14)	0.3613 (11)	0.6089 (18)	6.8 (18)	6.6 (12)	14.9 (28)	-2.8 (12)	1.4 (19)	-2.6 (14)
C(6)	0.2665 (16)	0.2886 (11)	0.4513 (17)	8.2 (21)	5.5 (11)	12.0 (27)	-1.3 (13)	0.1 (19)	-0.4 (13)
C(7)	0.1062 (15)	0.1950 (11)	0.5970 (18)	10.0 (21)	6.3 (11)	13.6 (28)	0.6 (12)	0.4 (20)	5.0 (15)
C(8)	0.2344 (15)	0.1176 (11)	0.4500 (16)	8.9 (20)	5.1 (11)	12.4 (25)	-0.2 (12)	3.0 (18)	1.8 (13)
C(9)	-0.0258 (15)	0.0014 (10)	0.2930 (19)	9.8 (20)	5.1 (10)	28 (4)	1.7 (11)	9.5 (23)	4.8 (15)
C(10)	-0.3288 (15)	-0.0569 (10)	0.0784 (19)	14.0 (23)	4.8 (10)	25 (3)	-3.8 (12)	7.4 (23)	3.7 (15)
C(11)	-0.3591 (20)	0.1216 (13)	0.4103 (23)	27 (4)	10.6 (16)	32 (4)	3.6 (18)	24 (3)	9.5 (21)
C(12)	-0.5571 (16)	0.3720 (15)	-0.1548 (22)	10.8 (21)	16.7 (19)	32 (4)	1.3 (17)	-4.0 (24)	17.7 (25)
C(13)	-0.4610 (17)	0.1248 (13)	-0.2211 (17)	16.1 (27)	12.9 (17)	12.1 (26)	-3.6 (17)	6.0 (23)	-4.8 (17)
C(14)	-0.6498 (17)	0.3017 (13)	0.0800 (22)	11.1 (23)	11.3 (16)	34 (4)	-3.4 (16)	13.0 (28)	1.2 (21)
C(15)	-0.2629 (15)	0.3991 (9)	0.4570 (16)	12.1 (20)	3.8 (9)	11.6 (23)	2.2 (11)	5.7 (19)	0.2 (12)
C(16)	-0.3555 (16)	0.3736 (12)	0.5053 (21)	16.5 (26)	8.6 (13)	32 (4)	3.8 (14)	19.3 (28)	8.1 (19)
C(17)	-0.1697 (16)	0.4448 (11)	0.5880 (19)	12.4 (24)	6.4 (12)	21 (3)	0.5 (14)	0.2 (23)	-5.8 (16)
C(18)	-0.3385 (16)	0.4546 (10)	0.3462 (16)	19.3 (26)	3.8 (9)	16.8 (27)	4.9 (12)	10.0 (22)	4.3 (13)
C(19)	-0.1135 (15)	0.3483 (10)	0.0010 (15)	15.3 (22)	4.5 (9)	11.4 (23)	-0.7 (12)	9.0 (19)	1.9 (12)
C(20)	0.0182 (15)	0.3719 (11)	0.0639 (18)	9.2 (20)	8.6 (13)	21 (3)	-4.4 (13)	5.4 (21)	4.2 (16)
C(21)	-0.2192 (15)	0.4269 (10)	-0.0525 (15)	16.2 (24)	6.0 (10)	10.6 (23)	-0.3 (12)	5.1 (20)	3.8 (12)
C(22)	0.1223 (15)	0.2622 (10)	-0.1212 (15)	17.3 (24)	5.2 (10)	10.2 (22)	-0.5 (12)	7.7 (20)	0 (12)

a Estimated standard deviations in the least significant figure(s) are given in parentheses in this and subsequent tables. b The form of anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The thermal coefficients are multiplied by 10^4.
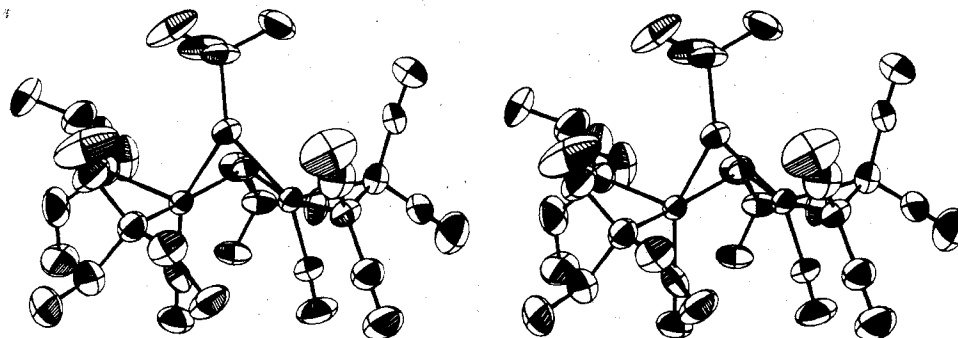

Figure 1. A stereoscopic view of $[Ir(\mu\text{-S-}t\text{-Bu})(CO)(P(OMe)_3)]_2[C(CN)_2]_2$.

agreement. The cell constants and corresponding standard deviations in Table I were obtained from a least-squares refinement of the setting angles of 25 reflections centered on a CAD4-Nonius computer-controlled diffractometer. Table I gives pertinent details about data collection conditions. Among the 4224 reflections, 2726 are unique and have $F^2 \geq 3\sigma(F^2)$ and only these reflections were used in subsequent refinement.

Initially it was assumed that the correct space group is the centrosymmetric one $P\bar{1}$, rather than its noncentrosymmetric subgroup $P1$. From the Patterson function, the Ir and S atoms were located, and on a subsequent difference Fourier map almost all atoms were found. Atomic scattering factors for all nonhydrogen atoms were taken from the usual tabulations.[5] Anomalous dispersion terms for Ir, S,

and P atoms were included in F_o.[6]

The refinement converged to $R = 0.026$ and $R_w = 0.029$ when all atoms were given an anisotropic thermal parameter. The final positional and thermal parameters of all atoms appear in Table II. A listing of the observed and calculated structure amplitudes is available.[7]

The low value of the R factor (0.026), together with the fact that the vibrational ellipsoids of all atoms within the molecule are quite normal, proves the correctness of the space group $P\bar{1}$ used in our calculation.

Results and Discussion

The addition of tetracyanoethylene to the complexes [Ir-

(5) D. T. Cromer and J. T. Waber, "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, Table 2.2.4.; D. T. Cromer, *ibid.*, Table 2.3.1.

(6) J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, **17**, 781 (1964).
(7) See paragraph at end of paper regarding supplementary material.

Table III. Selected Bond Distances (Å) for
[Ir(μ-S-t-Bu)(CO)(P(OMe)$_3$)][C(CN)$_2$]$_2$

Ir(1)–Ir(2)	2.679 (1)	C(15)–C(16)	1.575 (20)
Ir(1)–S(1)	2.384 (3)	C(15)–C(17)	1.513 (20)
Ir(1)–S(2)	2.419 (3)	C(15)–C(18)	1.510 (18)
Ir(1)–P(1)	2.252 (4)	C(19)–C(20)	1.552 (19)
Ir(1)–P(2)	2.301 (4)	C(19)–C(21)	1.546 (18)
Ir(1)–C(1)	1.888 (17)	C(19)–C(22)	1.545 (18)
Ir(2)–S(1)	2.393 (3)	C(3)–C(4)	1.518 (18)
Ir(2)–S(2)	2.357 (3)	C(3)–C(5)	1.469 (19)
Ir(2)–C(2)	1.855 (15)	C(3)–C(6)	1.471 (20)
Ir(2)–C(3)	2.130 (14)	C(4)–C(7)	1.437 (21)
Ir(2)–C(4)	2.098 (13)	C(4)–C(8)	1.452 (19)
P(1)–O(3)	1.567 (9)	C(5)–N(1)	1.102 (17)
P(1)–O(4)	1.580 (10)	C(6)–N(2)	1.139 (19)
P(1)–O(5)	1.590 (10)	C(7)–N(3)	1.144 (18)
P(2)–O(6)	1.546 (11)	C(8)–N(4)	1.127 (16)
P(2)–O(7)	1.571 (10)	O(3)–C(9)	1.482 (15)
P(2)–O(8)	1.580 (11)	O(4)–C(10)	1.470 (15)
S(1)–C(15)	1.905 (13)	O(5)–C(11)	1.423 (18)
S(2)–C(19)	1.880 (13)	O(6)–C(12)	1.457 (16)
C(1)–O(1)	1.132 (16)	O(7)–C(13)	1.480 (17)
C(2)–O(2)	1.132 (15)	O(8)–C(14)	1.390 (17)

Table IV. Selected Bond Angles (Deg) for
[Ir(μ-S-t-Bu)(CO)(P(OMe)$_3$)]$_2$[C(CN)$_2$]$_2$

S(1)–Ir(1)–S(2)	78 (1)	S(1)–Ir(2)–S(2)	79.2 (1)
S(1)–Ir(1)–P(1)	89.1 (1)	S(1)–Ir(2)–C(2)	153.5 (5)
S(1)–Ir(1)–P(2)	112.8 (1)	S(1)–Ir(2)–C(3)	108.0 (4)
S(1)–Ir(1)–C(1)	148.1 (5)	S(1)–Ir(2)–C(4)	97.1 (4)
S(2)–Ir(1)–P(1)	162.1 (1)	S(2)–Ir(2)–C(2)	98.3 (5)
S(2)–Ir(1)–P(2)	98.1 (1)	S(2)–Ir(2)–C(3)	126.9 (4)
S(2)–Ir(1)–C(1)	100.6 (4)	S(2)–Ir(2)–C(4)	166.9 (4)
P(1)–Ir(1)–P(2)	94.3 (2)	C(2)–Ir(2)–C(3)	94.6 (6)
P(1)–Ir(1)–C(1)	90.2 (4)	C(2)–Ir(2)–C(4)	90.5 (6)
P(2)–Ir(1)–C(1)	98.9 (5)	C(3)–Ir(2)–C(4)	42.1 (5)
Ir(1)–S(1)–Ir(2)	68.21 (9)	Ir(1)–S(2)–Ir(2)	68.23 (9)
Ir(1)–S(1)–C(15)	120.8 (5)	Ir(1)–S(2)–C(19)	122.3 (5)
Ir(2)–S(1)–C(15)	126.8 (5)	Ir(2)–S(2)–C(19)	117.5 (5)
Ir(1)–P(1)–O(3)	119.5 (4)	Ir(1)–P(2)–O(6)	108.3 (5)
Ir(1)–P(1)–O(4)	109.6 (4)	Ir(1)–P(2)–O(7)	118.9 (4)
Ir(1)–P(1)–O(5)	114.7 (4)	Ir(1)–P(2)–O(8)	115.5 (5)
Ir(1)–C(1)–O(1)	174 (1)	Ir(2)–C(2)–O(2)	177 (1)
Ir(2)–C(3)–C(4)	67.8 (8)	Ir(2)–C(4)–C(3)	70.1 (8)
Ir(2)–C(3)–C(5)	122 (1)	Ir(2)–C(4)–C(7)	120 (1)
Ir(2)–C(3)–C(6)	116 (1)	Ir(2)–C(4)–C(8)	119 (1)
C(4)–C(3)–C(5)	117 (1)	C(3)–C(4)–C(7)	114 (1)
C(4)–C(3)–C(6)	118 (1)	C(3)–C(4)–C(8)	118 (1)
C(5)–C(3)–C(6)	111 (1)	C(7)–C(4)–C(8)	111 (1)
P(2)–O(6)–C(12)	127 (1)	P(1)–O(3)–C(9)	121.6 (9)
P(2)–O(7)–C(13)	122 (1)	P(1)–O(4)–C(10)	122.1 (9)
P(2)–O(8)–C(14)	133 (1)	P(1)–O(5)–C(11)	129 (1)
S(1)–C(15)–C(16)	101 (1)	S(2)–C(19)–C(20)	107 (1)
S(1)–C(15)–C(17)	106 (1)	S(2)–C(19)–C(21)	102 (1)
S(1)–C(15)–C(18)	116 (1)	S(2)–C(19)–C(22)	113 (1)
C(3)–C(5)–N(1)	178 (2)	C(4)–C(7)–N(3)	177 (2)
C(3)–C(6)–N(2)	178 (2)	C(4)–C(8)–N(4)	178 (2)
O(3)–P(1)–O(4)	105.5 (5)	O(6)–P(2)–O(7)	106.7 (6)
O(3)–P(1)–O(5)	101.3 (6)	O(6)–P(2)–O(8)	106.4 (7)
O(4)–P(1)–O(5)	104.9 (6)	O(7)–P(2)–O(8)	100.0 (6)
C(16)–C(15)–C(17)	109 (1)	C(20)–C(19)–C(21)	112 (1)
C(16)–C(15)–C(18)	109 (1)	C(20)–C(19)–C(22)	113 (1)
C(17)–C(15)–C(18)	115 (1)	C(21)–C(19)–C(22)	109 (1)

(μ-S-t-Bu)(CO)(PR$_3$)]$_2$ (**1**) (R = Me, Ph, OMe) in dichloromethane solutions irreversibly yields dinuclear 1/1 adducts [Ir(μ-S-t-Bu)(CO)(PR$_3$)]$_2$[C(CN)$_2$]$_2$ (**2**).

Description of the Crystal and Molecular Structure of [Ir-(μ-S-t-Bu)(CO)(P(OMe)$_3$)]$_2$[C(CN)$_2$]$_2$. The crystal structure of [Ir(μ-S-t-Bu)(CO)(P(OMe)$_3$]$_2$[C(CN)$_2$]$_2$ consists of the packing of two dinuclear molecules. There is no close contact (<3 Å) between dinuclear molecules. Stereoscopic and perspective views of the molecule are shown in Figures 1 and 2,

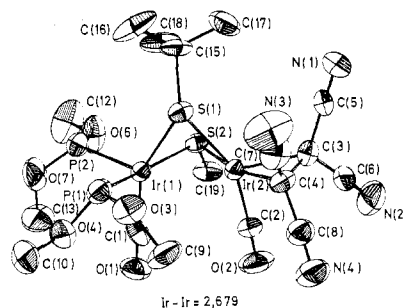**Figure 2.** Perspective view and labeling scheme of the molecule [Ir(μ-S-t-Bu)(CO)(P(OMe)$_3$)]$_2$[C(CN)$_2$]$_2$. The methyls of one of the t-Bu groups as well as atoms O(5), C(11), O(8), and C(14) and hydrogen atoms have been omitted for clarity.
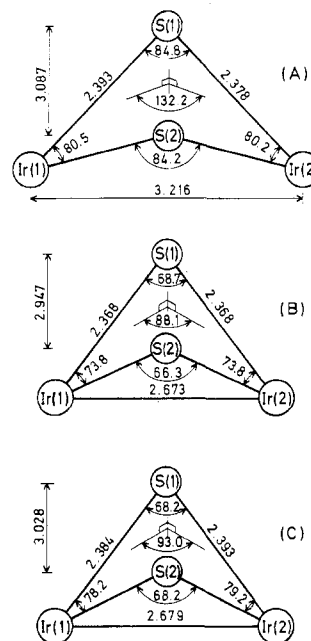

Figure 3. Schemes of the Ir$_2$S$_2$ four-membered rings A, B, and C, in compounds **1**, **3**, and **2**, respectively.

respectively. Figure 2 also indicates the labeling of the atoms. Bond distances are given in Table III and bond angles in Table IV.

In the dinuclear molecule, the iridium atoms are bridged by two thiolato ligands which are mutually anti. The Ir–Ir separation is 2.679 (1) Å, and the dihedral angle between the two planes containing [Ir(1)–S(1)–S(21)] and [Ir(2)–S(1)–S(2)] is 93°. These values clearly show an important compression of the Ir$_2$S$_2$ core along the Ir–Ir axis when they are compared with those of the starting material **1**, i.e., 3.216 (2) Å and 123.2°; moreover they are markedly similar to those found in the hydrogen adduct of **1**, i.e., [Ir(H)(μ-S-t-Bu)-(CO)(P(OMe)$_3$)]$_2$ (**3**)[4b] as it appears in Figure 3.

The Ir–S distances, in these three compounds, are not really significantly different, their mean values being 2.39, 2.39, and 2.41 Å for **1**, **2**, and **3**, respectively. The Ir–S–Ir angles of 68.21 (9) and 68.23 (9)° in **2** compare well with the values observed in **3**, i.e., 68.7 (1) and 66.3 (1)°, and contrast to the values of 84.7 (3) and 84.1 (3)° observed in the starting compound **1**. So the important decrease of the Ir–Ir distance, passing from **1** to its tetracyanoethylene adduct, mainly arises from a decrease of 30° in the flap angle without other significant modification in the Ir$_2$S$_2$ core parameters. These tendencies are similarly observed when we pass from **1** to **3** and have been already attributed to the metal–metal bond formation.[4b]

Let us consider now the environments of the iridium atoms

Table V. IR[a] and NMR[b] Data for [Ir(μ-S-t-Bu)(CO)(PR$_3$)]$_2$[C(CN)$_2$] Complexes

R	ν(CO)	ν(CN)	τ(R)	$^3J_{PH}$	τ(t-Bu)	δ(^{31}P{^{1}H})	$^2J_{PP}$
OMe	2027 vs	2218 sh	6.17 (d, isomer α)	11.5	8.57 (s)	73.26 (d)	26.8
	1993 m	2212 m			8.54 (s)	57.49 (d)	26.8
			6.17 (d, isomer β)	11.3	8.57 (s)	72.98 (d)	29.8
					8.55 (s)	57.24 (d)	29.8
	2025 s[c]	2217 sh[c]					
	1987 m	2207 m					
Ph	2023 vs	2216					
	2002 m						
Me	2015 vs	2215	7.87 (d)	9.1	8.58 (s)		
	1995 m				8.48 (s)		

[a] CH$_2$Cl$_2$ solution; cm^{-1}. [b] CH$_2$Cl$_2$ or CD$_2$Cl$_2$ solution; τ and δ values ±0.02; J values ±0.2 Hz. [c] Recorded as CsBr pellets.

Ir(1) and Ir(2). Ir(2) is bonded to two sulfur atoms of the *tert*-butyl thiolato bridging groups, one carbon of a carbonyl, and two carbons of tetracyanoethylene. The distances between Ir(2) and ethylenic carbons C(3) and C(4) of 2.130 (14) and 2.098 (13) Å are slightly shorter than those typically observed in IrBr(CO)(PPh$_3$)$_2$(TCNE) (2.15 Å)[8a] and in Ir(C$_6$N$_4$H)-(CO)(PPh$_3$)$_2$(TCNE) (2.18 Å).[8b] The C$_6$N$_4$ unit of the TCNE ligand is not planar, the dihedral angle between the two planes [C(3),C(5),C(6)] and [C(4),C(7),C(8)] being 105°. The C(3)–C(4) bond length is 1.518 (18) Å. All these values, in the range observed for tetracyanoethylene complexes of Ni, Pt, or Ir[9] are thus consistent with a considerable electron transfer from the metal to the electrophilic olefin. Ir(1) is bonded to two sulfur atoms of the *tert*-butyl thiolato bridging group, one carbon of a carbonyl group, and two phosphorus atoms of trimethyl phosphite ligands; dihedral angles formed by the normals to adjacent polytopal faces[10] (Table V) indicate a geometry around Ir(1) intermediate between idealized trigonal bipyramid and tetragonal pyramid. The Ir(1)–P(2) bond distance of 2.301 (4) Å is significantly longer than the Ir(1)–P(1) bond of 2.252 (4) Å. We correlate this lengthening to the presence of an Ir–Ir bond roughly in trans position toward the Ir(1)–P(2) bond. All Ir–C and C≡O observed bond distances are quite normal.

Taking into account the ligand environments, it appears that Ir(1) is an electron-rich metal center while Ir(2) is an electron-deficient metal center. A heteropolar homonuclear metal–metal bonding is thus required to explain the short Ir(1)–Ir(2) distance of 2.679 (1) Å analogous to that proposed for Ir(η^5-C$_5$H$_5$)Ir(CO)$_2$(CF$_3$C$_2$CF$_3$)$_2$H in which the Ir–Ir distance is equal to 2.737 (1) Å.[11] Such a metal–metal-bonding type has recently been suggested.[12-14] This metal–metal bond allows an electronic charge transfer from the electron-rich Ir(1) center to the electron-deficient Ir(2) center. From this point of view, it is of interest to consider the infrared spectrum of the isomorphous crystal. It exhibits two CO stretching bands (in CsBr pellets) at 2025 and 1987 cm^{-1}. With no interaction between the two metallic centers, we would rather expect a spacing of at least 100 cm^{-1} between the two CO stretching bands. Indeed, (i) the introduction of tetracyanoethylene would normally be accompanied by an increase of ca. 90 cm^{-1} for the stretching frequency of CO on Ir(2),[15] the geometry of the tetracyanoethylene ligand being consistent with a strong electron-attractive behavior, (ii) further addition

of a phosphite ligand on Ir(1) should be accompanied by a decrease of the stretching frequency of the CO group on this metal atom, and (iii) the possible coupling between the two CO groups should induce an increase of the splitting. Therefore, the rather small observed spacing can only be explained if an important electronic transfer occurs from Ir(1) to Ir(2) via a coordinate covalent metal–metal bond.

Structure in Solution. From NMR and IR data (Table V), we postulate that all the prepared compounds [Ir(μ-S-t-Bu)(CO)(P(R)$_3$)]$_2$[C(CN)$_2$]$_2$ have an analogous structure and that this structure is preserved in solution.

The NMR data of [Ir(μ-S-t-Bu)(CO)(P(OMe)$_3$)]$_2$[C-(CN)$_2$]$_2$ indicate the existence of two isomeric forms designated as α and β. The ^{31}P{^{1}H} spectrum shows, for isomer α, two doublets of equal intensites at δ 73.26 (30%) and 57.49 ppm (30%) with doublet spacing of 26.8 Hz and, for isomer β, two doublets of equal intensities at δ 72.98 (20%) and 57.24 (20%) with doublet spacing of 29.8 Hz. These data indicate the presence of two nonequivalent phosphite ligands in each isomer, and the multiplicity of the signals indicates a coupling between cis phosphorus nuclei.[15] This spectrum is invariant with temperture in the range −70 to +35 °C.

As for the methyl protons of the phosphite ligands, the ^{1}H NMR spectra show, at ambient temperature and at −70 °C, two doublets of unequal intensities, separated by 0.4 Hz (at 60 MHz), according to the existence of two isomeric forms. In the *tert*-butyl region, the spectra exhibit three signals at τ 8.54 ($\sim$30%), 8.55 ($\sim$20%), and 8.57 ($\sim$50%). This result indicates nonequivalent *tert*-butyl groups for isomers α and β, i.e., for isomer α, τ(t-Bu) 8.54 and 8.57 ($\sim$30% for each singlet) and, for isomer β, τ(t-Bu) 8.55 and 8.57 ($\sim$20% for each singlet).

It is noteworthy that the similarity and the vicinity of the signals of each isomer in the ^{1}H as well as in the ^{31}P{^{1}H} NMR spectra strongly suggest geometries which must differ only by small changes, like endo to exo permutation of one *tert*-butyl group.

Registry No. **1** (R = OMe), 63292-76-2; **1** (R = Me), 63292-79-5; **1** (R = Ph), 63264-36-8; **2** (R = OMe), 74097-08-8; **2** (R = Me), 74097-09-9; **2** (R = Ph), 74097-10-2.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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